Tampere University

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ACADEMIC DISSERTATION
To be presented, with the permission of
the Faculty of Engineering and Natural Sciences
of Tampere University,
for public discussion in the TAU SA203 S2 auditorium
of the Sähkötalo, Korkeakoulunkatu 3, Tampere,
on 5 December 2019, at 12 o'clock.

ACADEMIC DISSERTATION
Tampere University, Faculty of Engineering and Natural Sciences
VTT Technical Research Centre of Finland Ltd
Finland

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The originality of this thesis has been checked using the Turnitin OriginalityCheck service.

Cover design: Roihu Inc.

ISBN 978-952-03-1362-3 (print)
ISBN 978-952-03-1363-0 (pdf)
ISSN 2489-9860 (print)
ISSN 2490-0028 (pdf)
http://urn.fi/URN:ISBN:978-952-03-1363-0

PunaMusta Oy – Yliopistopaino
Tampere 2019

Dedication

This PhD Thesis is dedicated to my grandfather "Faffa", who passed away at the age of 89 during my final writing process. He, among others in my family, had a career in forest industry, and I am lucky to cross over this path. Rest in peace with Fammu.

PREFACE

The work presented in this thesis has been conducted at VTT Technical Research Centre of Finland Ltd., in the Department of Biomass Processing and Products. The work was part of research projects BIOSTRUCT (2008-2012, funded by European Commission Framework 7), CLIC New Fibre Products (2014-2018, funded by CLIC Innovation Ltd.), as well as VTT internal project RFC Upgradation (2013). XPS measurements of the Publication I were performed by Aalto School of Chemical Engineering, Department of Bioproducts and Biosystems.

I am very thankful to my supervisor Prof. Jyrki Vuorinen for the guidance and conversations during finalisation of the thesis, and my instructor, Principal Investigator David Sandquist (VTT) for the valuable instructions and comments to the dissertation. I would also like to express my gratitude to the opponent and pre-examiners of the thesis.

I thank all my co-authors for contributing to the publications. In addition, I want to acknowledge VTT for giving me the tools and support to finalise my PhD, as well as the possibility to work in several projects during these years. I am especially thankful to my Research Team leader Lisa Wikström, who has always believed in my talents, and our Head of Research Area Jani Lehto. I am lucky to have numerous wise and helpful colleagues, and I am particularly grateful to my past and current co-workers Elina Pääkkönen, Kalle Nättinen, Kirsi Immonen, Petri Jetsu, Teijo Rokkonen, Hannu Minkkinen, Tero Malm, Mirja Nygård and Sini-Tuuli Rauta. I also thank my colleagues and friends Elina Yli-Rantala, Marjaana Karhu and Sanna Mikkola for all the conversations as my peer-supports in PhD studies.

I also want to thank my parents and my three siblings, whom I learned to appreciate more and more as an adult: thank you for being there. Last, but definitely not least, I thank my dear husband Samuli for holding my hand through Hell (and back), and my two lovely daughters: Laulu, my bright star, talented and smart, and Muusa, my inspiration with all the energy and open-minded attitude. I love you all.

Tampere

Heidi Peltola

ABSTRACT

Increasing environmental awareness and tightening EU legislations have gained significant interest towards bio-based material solutions. Lignocellulosic fibre reinforced biocomposites can provide a sustainable material alternative for several plastic products. In biocomposites, renewable raw material sources, such as wood fibres, replace typically fossil-based resources, often decreasing also the carbon footprint of the material. Utilisation of wood fibres also provide additional material improvements to plastics, such as increased mechanical performance and natural haptics. However, while biocomposite materials can be mechanically recycled, building up an economically viable municipal recycling system is challenging due to low material volumes and heterogeneous material streams. Thus, biocomposites based on biodegradable or compostable matrix materials can complement the circular economy by providing an alternative end-of-life solution for products that are not applicable for recycling, but on the other hand, not excluding recyclability.

This thesis concentrates on the effects of wood fibre morphologies on biocomposite performance using compostable poly(lactic acid) (PLA) as the matrix material. The main objective was to increase knowledge of the factors influencing the material characteristics to enable their wider use in commercial applications. To reach this objective, the study focused especially to the effect of melt processing on fibre morphologies, as well as the effect of various fibre surface treatments and fibre selection on performance of injection moulded bicomposites. Particular attention was paid to fibre attrition, dispersion and their correlation to mechanical performance. In addition, new light-weight application areas were considered by evaluating the effect of fibre addition on PLA foamability in extrusion foaming process.

As a conclusion, it was observed that melt processing of wood fibres with PLA has unpreventable effect on wood fibre morphology. All selected bleached wood fibre types shortened to the same level independent of the initial fibre length while fibre diameters remained unchanged. Thus, aspect ratio depended on retaining fibre length and initial fibre width of the fibres. Industrial fibre bleaching was found to be

one factor influencing the increased fibre attrition due to higher refinability of bleached fibres. However, due to differences in fibre dispersion, no straight conclusions could be made of the correlation between fibre aspect ratio after processing and the mechanical properties of the composites. On the other hand, fibre dispersion and fines content seemed to partly reflect the mechanical performance. Improved mechanical properties were obtained by utilisation of unbleached hardwood kraft pulp fibres with low fibre attrition during processing, thermomechanical pulp, fibre fractionation or addition of compatibiliser/dispersing agent to the system. The presence of lignin and epoxidated linseed oil also indicated improvement in fibre-matrix adhesion. The work also presented that recycled fibres, such as non-deinked newspapers and liquid packaging board scratch, have potential to be used as PLA reinforcement. In extrusion foaming process, addition of wood fibres to PLA still enabled the production of low-density foams with decreased cell size and increased cell density. As an overall conclusion, careful selection of fibre type and treatments can provide significantly improved properties for wood fibre reinforced PLA biocomposites.

TIIVISTELMÄ

Kasvavan ympäristötietoisuuden ja EU:n lainsäädännön myötä biopohjaiset materiaaliratkaisut kiinnostavat entistä enemmän. Lignoselluloosapohjaiset kuitulujitetut biokomposiitit voivat tarjota ympäristöystävällisen materiaalivaihtoehdon monille erilaisille muovituotteille. Biokomposiiteissa fossiilisista lähteistä peräisin olevaa materiaalia korvataan uusiutuvilla raaka-ainelähteillä, kuten puukuiduilla, joka usein myös laskee tuotteen hiilijalanjälkeä. Puukuitujen käyttö voi parantaa myös materiaalin muita ominaisuuksia, kuten mekaanisia ja haptisia piirteitä. Biokomposiitteja voi myös kierrättää mekaanisesti, mutta taloudellisesti kannattavan kierrätyssysteemin rakentaminen on vaikeaa biokomposiittien toistaiseksi alhaisen volyymin ja jakeiden heterogeenisuuden vuoksi. Sen vuoksi biokomposiitit, jotka pohjautuvat biohajoaviin tai kompostoituviin materiaaleihin, voivat tukea kiertotaloutta tarjoamalla vaihtoehtoisen käsittelytavan tuotteille, jotka eivät sovi kierrätykseen. Toisaalta näiden materiaalien kierrättäminen ei ole poissuljettua.

Tässä väitöskirjassa keskitytään puukuitujen morfologian vaikutukseen polylaktidi (PLA) –pohjaisten biokomposiittien ominaisuuksiin. Työn päätavoite oli luoda lisää tietoa näiden materiaalien ominaisuuksiin vaikuttavista tekijöistä, jonka kautta materiaalien laajempi kaupallinen hyödynnettävyys lisääntyy. Tavoitteen saavuttamiseksi tutkimuksessa keskityttiin erityisesti siihen, miten materiaalien sulatyöstö vaikuttaa kuitujen morfologiaan sekä siihen, miten kuidun valinta ja erilaiset kuidun pinnan muokkaukset vaikuttavat ruiskuvalettujen biokomposiittien ominaisuuksiin. Työssä kiinnitettiin erityisesti huomiota kuidun pilkkoontumiseen, dispersioon ja niiden riippuvuuteen komposiitin mekaanisesta suorituskyvystä. Näiden lisäksi työssä tarkasteltiin uusia kevyitä sovellusalueita arvioimalla kuidun lisäyksen vaikutusta PLA:n vaahtoavuuteen ekstruusiovaahdotusprosessissa.

Työssä todettiin, että puukuitujen sulatyöstö PLA:n kanssa vaikuttaa väistämättä kuitujen morfologiaan. Kaikki valitut puukuitutyypit lyhenivät samalle tasolle riippumatta kuidun alkuperäisestä pituudesta, kun taas kuitujen halkaisija pysyi muuttumattomana. Näin ollen kuitujen pituus/leveyssuhde oli riippuvainen kuitujen

loppupituudesta ja lähtöleveydestä. Kuitujen teollinen valkaisu näytti olevan yksi kuidun tuhoutumiseen vaikuttaneista tekijöistä, sillä valkaistu kuitu on ominaisuuksiltaan helpommin jauhautuvaa. Kuitudispersioiden eroavaisuuden vuoksi suoria johtopäätöksiä kuidun pituus/leveyssuhteen ja komposiitin mekaanisten ominaisuuksien välillä ei voitu kuitenkaan tehdä. Toisaalta kuitujen dispersio ja hienoainepitoisuus näyttivät osittain peilaavan komposiitin mekaanista suorituskykyä. Komposiittien ominaisuudet paranivat käyttämällä lujitteena valkaisematonta sellukuitua, joka säilytti paremmin mittansa sulatyöstön aikana, sekä käyttämällä termomekaanista sellua, fraktioitua kuitua tai dispergointi-/ kompatibilisointiainetta. Pintaligniini ja epoksoitu pellavansiemenöljy näyttivät parantavan myös kuidun ja matriisin välistä yhteensopivuutta. Työssä todettiin myös, että kierrätyskuiduilla, kuten siistaamattomilla sanomalehdillä ja nestepakkauskartongilla, on potentiaalia PLA:n kuitulujitteena. Ekstruusiovaahdotuksessa kuidun lisäys mahdollisti keveiden vaahtojen valmistamisen. Kuitulisäyksellä saavutettiin pienempi solukoko ja suurempi solutiheys kuin puhtaalla PLA:lla. Kaiken kaikkiaan työn yhteenvetona voidaan todeta, että oikealla kuidunvalinnalla ja kuitukäsittelyillä voidaan saavuttaa merkittävä parannus puukuitulujitteisten PLA-biokomposiittien suorituskykyyn.

CONTENTS

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

BHKP	Bleached hardwood kraft pulp from birch
BHKP-e	Bleached hardwood kraft pulp from eucalyptus
BSKP	Bleached softwood kraft pulp (derived from spruce and pine)
CO_2	Carbon dioxide
DSC	Differential scanning calorimetry
d.s.c.	Dry solid content
FS	Fibre sludge
HPAEC	High-performance anion-exchange cromatography
ELO	Epoxidated linseed oil
EPX	Bifunctional organosilane with epoxide and triethoxysilyl group
LPB	Liquid packaging board
MAH	Maleic anhydride
MAPP	Maleic anhydride grafted polypropylene
ONP	Old newspaper
PE	Polyethylene
PEG	Poly(ethylene glycol)
PLA	Poly(lactic acid)
PDLLA	Copolymer of poly(*D,L*-lactic acid)
PDLA	Isotactic homopolymer of poly(*D*-lactic acid)
PLLA	Isotactic homopolymer of poly(*L*-lactic acid)
PP	Polypropylene
PVC	Polyvinyl chloride
PVA	Poly(vinyl acetate) based binder
rpm	rounds per minute
SEC	Specific energy consumption
SEM	Scanning electron microscope
SIL	Silicon reinforced polyether-based silane-terminated polymer

TMP	Thermomechanical pulp
T_g	Glass transition temperature
T_m	Melting temperature
UHKP	Unbleached hardwood kraft pulp from birch
WF	Wood flour
WPC	Wood Plastic Composite
XPS	X-ray photoelectron spectroscopy

SYMBOLS

l_c	Critical fibre length
d	Diameter
σ_f^*	fibre tensile strength
τ_c	fibre-matrix bond strength or the shear yield strength of the matrix, if it is smaller
wt-%	Weight percent

ORIGINAL PUBLICATIONS

Publication I Peltola, Heidi; Immonen, Kirsi; Johansson, Leena-Sisko; Virkajärvi, Jussi; Sandquist, David. Influence of pulp bleaching and compatibiliser selection on performance of pulp fibre reinforced PLA biocomposites. Journal of Applied Polymer Science 136 (37) (2019) 47955.

Publication II Peltola, Heidi; Pääkkönen, Elina; Jetsu, Petri; Heinemann, Sabine. Wood based PLA and PP composites: Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties. Composites: Part A. 61 (2014) 13-22.

Publication III Peltola, Heidi; Laatikainen, Elina; Jetsu, Petri. Effects of physical treatment of wood fibres on fibre morphology and biocomposite properties. Plastics, Rubber and Composites 40 (2) (2011), 86-92.

Publication IV Pääkkönen, Elina; Wikström, Lisa; Peltola, Heidi; Valta, Kyösti; Retulainen, Elias. Recycled fibres and fibrous sludge as reinforcement materials in injection moulded polypropylene (PP) and poly(lactic acid) (PLA) composites. Journal of Bioresources and Bioproducts 2(3) (2017), 116-122.

Publication V Rokkonen, Teijo; Peltola, Heidi; Sandquist, David. Foamability and viscosity behaviour of extrusion foamed PLA - pulp fiber composites. Journal of Applied Polymer Science 136 (41) (2019) 48202.

AUTHOR'S CONTRIBUTION

Publication I Author planned the experiments, interpreted the results except for XPS measurements and acted as main author of the publication. All authors took part in writing of the article, and commented and approved the manuscript.

Publication II Author was the main responsible person of planning biocomposite processing and testing, interpreted the results relating to biocomposites and acted as main author of the publication. All authors took part in writing of the article, and commented and approved the manuscript.

Publication III Author was the main responsible person of planning biocomposite processing and testing, interpreted the results and acted as main author of the publication. All authors took part in writing of the article, and commented and approved the manuscript.

Publication IV Author interpreted the results together with other authors, and acted as co-author of the publication. All authors took part in writing of the article, and commented and approved the manuscript.

Publication V Author planned the experiments with the main author, interpreted the results relating to wood fibre reinforcement and acted as co-author of the publication. All authors took part in writing of the article, and commented and approved the manuscript.

1 INTRODUCTION

Detaching from a dependency on fossil-based resources is one of the main climate targets in the European Union. [1] Within the target to decarbonise Europe, the strategy for climate-neutral economy provides a vision of economic and societal transformations by reducing energy consumption and taking full benefit from bio- and circular economy. While bio-based materials support the transition towards renewable resources, composites with improved performance as well as light-weight solutions fulfil the strategy by contributing to material savings, utilisation of bio-based reinforcements and lower energy consumption in logistics.

Composites are defined as materials that consist of more than one phase (multiphase materials). The phases must differ from each other and be separated by a distinct interphase. In general, composites can be divided into three main groups: particle-reinforced, fibre-reinforced and structural composites (Figure 1). In fibre reinforced composites, fibres can be either continuous or short fibres, having different reinforcing properties in the composite structure. [2]

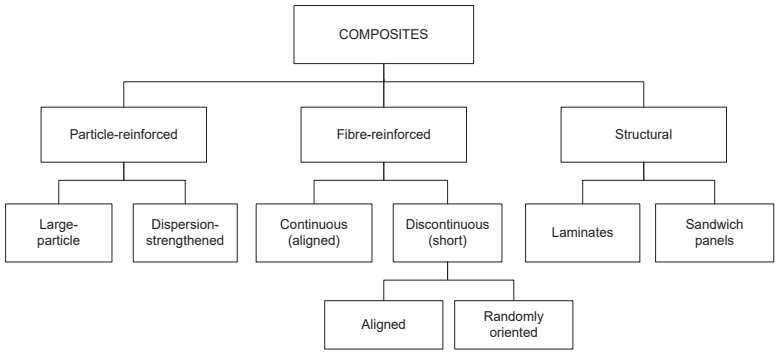


Figure 1. Composite classification according to reinforcing component

Biocomposites are composite materials in which at least one of its components is derived from natural resources. [3] In thermoplastic composites, the matrix phase surrounding the fibres is composed of a thermoplastic (polymer), i.e. thermally

mouldable, heat reversible, material. In conventional thermoplastic biocomposites, fossil-based plastic, normally polypropylene (PP), polyethylene (PE) or polyvinyl chloride (PVC), can be replaced up to 50-70 wt% by natural fibres; in case of wood plastic composites (WPC's), the natural reinforcement is based on wood. [4] Especially wood flour has been used as a filler in WPC's for decades in applications such as decking or fencing. Wood flour provides stiffness to the composite structure and enables the use of saw mill side streams as cheap filler replacing fossil-based plastic, but other properties are not typically improved. [5]

In recent years, several forest companies, as well as other businesses, have launched wood fibre based biocomposites to market instead of wood flour filled composites. [6–9] Wood fibres such as pulp fibres are able to provide improved properties to the composite structure, such as strength and impact resistance. Thus, wood-based biocomposites are nowadays found in various injection moulded products, such as furniture, loudspeakers, kitchenware, and design products (Figure 2). The materials are typically based on fossil-based polymers, but also bio-based drop-in plastics as matrix materials have found place on the market.

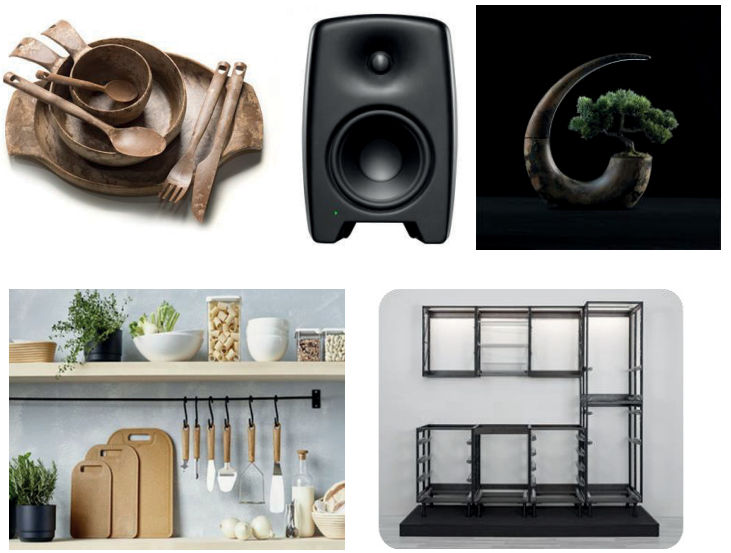


Figure 2. Various commercial wood fibre reinforced biocomposite products. Upper line: Kuplika by Plasthill Oy; Genelec loudspeakers produced from UPM Formi; Romolo Stanco's Green Lamp made from ARBOFORM by Tecnaro GmbH. Lower line: Orthex kitchen products from Stora Enso DuraSense; Puustelli ecokitchen from UPM Formi.

However, as the world is moving from linear to circular economy, the problem is that recycling of these biocomposite materials at their end-of life is currently challenging. Thermoplastic biocomposites from the material point-of- view can be recycled [10], but building up feasible logistics and sufficient, homogeneous streams for recycling on a municipal level is demanding due to alternating constituents. Therefore, in some applications, compostable material solutions can provide an alternative end-of-life possibility instead of incineration or landfilling.

Poly(lactic acid) (PLA) is currently one of the most available commercial biopolymer, manufactured in various grades and relatively high volumes. It is produced from lactic acid derived from starch-rich sources such as corn, and polymerised to be used in plastic products ranging from single-use cups, lids and packages to biocompatible implants, 3D filaments, breathable films, technical parts as well as low density foams. It is both bio-based and compostable, allowing for reduced carbon dioxide emissions together with alternative end-of life possibilities for incineration and recycling. [11,12] PLA can also be mechanically and chemically recycled. [13] However, it has not yet been widely applied in commercial biocomposite applications apart from cellulose fibre reinforced 3D filaments.

In research and development projects, the use of PLA based wood fibre composites have been demonstrated to be applicable for large injection moulded products, film production, thermoforming and extrusion foaming. However, more research is required to gain an understanding of general properties affecting the performance of the PLA – pulp fibre biocomposites. Specific attention should be paid to enlighten the factors that control the material properties, find fully bio-based compositions and tailor properties according to end-application to demonstrate the commercial potential. As material development will progress further, fossil-based materials can be replaced by bio-based plastics such as PLA, and the materials can be used for other applications such as thermoformable or extrusion foamable products, some of them demonstrated in Figure 3.

Figure 3. Future products from pulp fibre reinforced PLA composites, demonstrated by VTT

2 POLY(LACTIC ACID)

Poly(lactic acid) (PLA) is a commercial, bio-based polymer based on corn, sugarcane, tapioca or other starch-rich raw material source. PLA is also biodegradable and industrially compostable according to EN13432 standard. It belongs to family of aliphatic polyesters derived from α–hydroxy acids, and consists of lactic acid monomers, found in two stereochemical structures: *L*- and *D*-form (Figure 4.). These *L*- and *D*-lactic acids can form three different cyclic stereoisomers by dehydration of the two lactic acid molecules: D,D-lactide (*D*-lactide), L,L-lactide (*L*-lactide), and D,L-lactide (or meso-lactide). Rac-lactide, as one type of meso-lactide, is formed by equimolar mixture (1:1) of *L*- and *D*-lactide. [14] Due to the varying lactide forms, commercial PLA polymers are available as isotactic homopolymers of poly(*L*-lactic acid) (PLLA) and poly(*D*-lactic acid) (PDLA), as well as atactic copolymers of poly(*D,L*-lactic acid) (PDLLA) produced from *L*-lactic acid and *D,L*-lactic acid. [15]

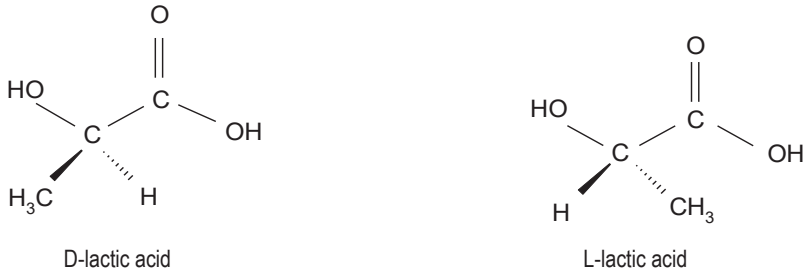


Figure 4. Chemical structures of lactic acid isomers

PLA polymers can be synthetised from the lactic monomers by several routes, including polycondensation, azeotropic dehydrative polycondensation, or ring-opening polymerization of lactide. The most commercial viable route to produce PLA is conversion of the cyclic lactide to PLA via ring-opening polymerization. [16] Polycondensation results in low molecular weight end-products without possibility to control the stereoregularity during polymerisation; thus, this method is used if low molecular weight PLA is required. [15] PLA degrades through hydrolysis of ester

linkages of the polymer backbone. The degradation in environmental conditions depend on material properties such as molecular weight, crystallinity and optical purity, as well as environmental conditions, such as temperature, humidity, pH, UV light, and type of microorganisms. [17]

Material properties of PLA depend highly on stereochemical structure of polymer backbone as well as molecular weight. In general, PLA is comparable to polystyrene (PS), with high modulus and tensile strength, and low ductility. Optically tactic *L*- and *D*-PLA polymers are semicrystalline with better mechanical and thermomechanical properties, while atactic, racemic PLA provides amorphous material typically used in biomedical applications. [18] Figure 5 represents stereoisomeric forms of PLA and their correlation to melting temperature (T_m) and crystallinity. Full stereocomplex PLA is formed by blending PLLA and PDLA in 50/50 ratio, enabling the formation of stereocomplex crystals with alternating helices instead of homochiral crystallisation. [19,20]

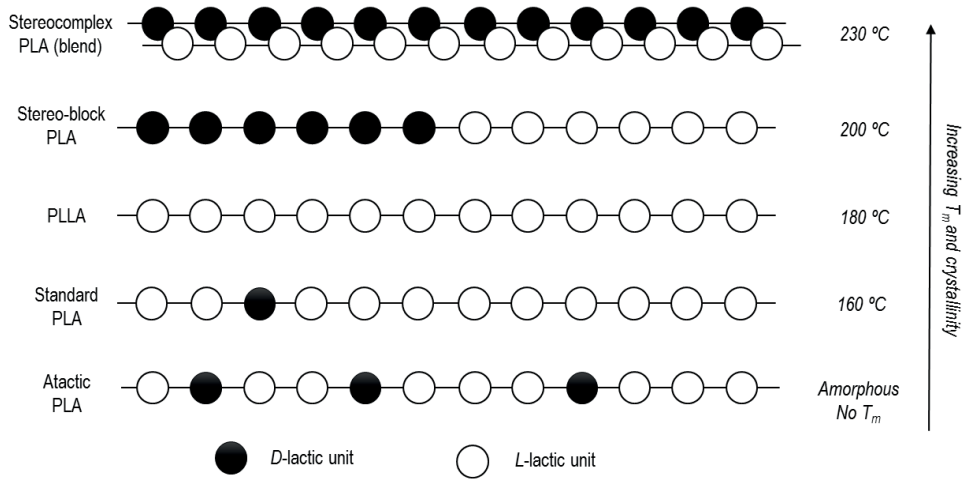


Figure 5. Stereoisomeric forms of PLA. Figure adapted from [20,21]

While PLA in general obtains good strength properties and film transparency, its drawbacks include low heat deflection temperature and brittleness. [22] Several methods have been presented in the literature to improve the physical performance of PLA, including plasticisation [23,24], blending [25], mineral fillers [26] and chain extension [27]. Commercial high heat PLA grades are already available, in which high

heat stability has been reached by crystallisation induction through nucleation [28] or stereo-chemical blends [29]. Stereocomplex structures enable high crystallinity with significantly improved thermal resistance. [19] Annealing (or thermal stabilisation) of processed PLA in elevated temperatures above glass transition temperature increases heat deflection and Vicat penetration of *L*-PLA from 55 to 61 °C and from 59 to 165 °C, respectively. [30] Mechanical and thermal characteristics of *D,L*-PLA and *L*-PLA with and without annealing are seen in Table 1., showing the effect of stereochemistry and crystallinity (induced by annealing) on PLA performance.

Table 1. PLA properties and the effect of stereochemistry and crystallinity [30]

Properties	L-PLA	L-PLA, annealed	D,L-PLA
Tensile strength (MPa)	59	66	44
Elongation at break (%)	7.0	4.0	5.4
Modulus of elasticity (MPa)	3750	4150	3900
Yield strength (MPa)	70	70	53
Flexural strength (MPa)	106	119	88
Unnotched izod impact (J/m)	195	350	150
Notched izod impact (J/m)	26	66	18
Rockwell hardness	88	88	76
Heat deflection temperature (°C)	55	61	50
Vicat penetration (°C)	59	165	52

Annual production rate of PLA in 2017 was over 212,000 tons and is predicted to grow to 321,000 tons by 2022. [31] The largest PLA producers are NatureWorks LCC (U.S.A) and Total Corbion PLA (The Netherlands). PLA is used in several product applications, including fibres, films, thermoformed products, polymer foams, technical parts and medical applications. Novel PLA production technologies, especially the economically viable production of *D*-PLA to achieve of full stereocomplex PLA, enables the use of PLA-based products also in applications requiring higher heat resistance. Due to high production volumes and latest developments, PLA is commercially available in several grades.

PLA can be processed with conventional processing methods, such as injection moulding, film and sheet extrusion, blow moulding, thermoforming, fibre spinning, as well as particle and extrusion foaming. [32] For successful processing, PLA needs to be carefully dried before processing to avoid thermal degradation through hydrolysis, which leads to loss of molecular weight and consequently to decreased

material performance. High processing temperatures or elongated residence times accelerate thermal degradation. [33] Typical processing temperatures for standard PLA are between 190-210 °C in extrusion, injection moulding and foaming. [33] Due to rather low melt strength of PLA caused by relatively low molecular weight and branching, foaming of PLA requires the use of chain extender to enable the production of low density foams. [34,35] High melt strength enables the forming cells to hold their shape and resist rupture before cell structure stabilisation, in addition to widening the processing window of PLA foams. [36]

3 WOOD-BASED FIBRES

Wood can be considered as a natural composite having complex macrostructure as well as intricate physical and chemical microstructure. [37] It consists of tubular cellulose fibres that are embedded in a matrix of hemicellulose and lignin. Wood fibre wall is built on several layers: middle lamella, primary wall, and a three-layered inner layer (secondary wall). The thin middle lamella, consisting mostly from lignin, ensures adhesion between the cells. Both the primary wall and inner layer surfaces are surrounded by crystalline microfibrils with varying alignments. [38,39] Cellulose is the dominant chemical component in wood fibres, typically measuring up to 40-45% of softwood and hardwood fibres, while lignin and hemicellulose are present around 25-35% and 20-30%, respectively. Most of the cellulose and hemicellulose are found in the three-layered inner secondary wall, while lignin is present both in middle lamella, primary wall and secondary walls. [40] The percentual contents differ depending on the wood source. [41] Typical wood fibre dimensions with respect to wood source are shown in Table 2.

Table 2. Fibre dimensions of various wood based fibres. The actual values depend on the specific species and collected sample. [42]

Fibre source	Fibre length, mm	Fibre width, µm	Aspect ratio
Hardwoods			
Acacia	0,8	14	60
Birch	1,3	25	52
Eucalyptus	1,1	20	53
European Aspen	0,9	19	47
Softwoods			
Balsam fir	3,5	30-40	100
European spruce	3.5	27	130
Radiata pine	2,8	37	76
Scots pine	3,6	39	92

In addition to fibre source, wood fibre properties also differ depending on the used separation method, known as pulping. Pulping releases cellulosic fibres from otherwise compact wood structure. Pulp fibres are mainly used for papermaking, but also processed into various cellulose derivatives and regenerated cellulose. [41] Pulping can be established either chemically, mechanically or semi-chemically. In mechanical pulping, cellulosic fibres are separated mechanically by softening the lignin either by grinding or refining. In mechanical pulps, all wood components stay in the pulped product, providing high yield for the process. However, due to harsh processing conditions, the fines content is relatively high. Within mechanical pulps, thermomechanical pulp (TMP), being one of the main mechanical pulp types, is produced by refining preheated wood chips under pressure at elevated temperatures. [37]

In chemical pulping, chemicals are used to dissolve and degrade lignin from the wood fibres. Using high temperature and pressure, 50% of wood material can be removed by chemical pulping means. [43] Within chemical pulping, kraft (sulfate) pulping is the most common pulping process currently in operation. [40] In kraft pulping, sodium hydroxide and sodium sulphite are used as active alkali, which react with lignin and promote dissolution of the lignin polymer. [44] Delignification process can be divided into three phases: initial, bulk and final (residual) delignification. The residual delignification results in pulp yield losses, thus the kraft cook is often stopped before or during the residual delignification: after the kraft pulping, unbleached kraft fibres contain 2-4.5% residual lignin. The residual lignin is the major contributor to the pulp fibre colour. Therefore bleaching is utilised to remove the remaining residual lignin to obtain a white cellulose pulp. In addition, bleaching reduces shives and bark debris, and dissolves pulp extractives. [45]

In addition to virgin pulp fibres, recycled paper or cardboard fibres can be utilised as an alternative for biocomposite reinforcement. [46–48] Especially the use of non-deinked fibrous materials can provide simple and affordable option, but the heterogeneous streams including chemicals, inks, adhesives and minerals might have an effect on the end-product. On the other hand, non-deinked newspaper fibres have shown improved properties as composite reinforcement due to coupling effect of ink particles and superior fibre properties compared to deinked fibres. [49] Virgin newspapers are typically produced from mechanical pulp, but as the utilisation rate

for recycled fibres in newsprint can be up to 100% in Europe, newspapers might include also other components such as other mechanical or chemical pulp fibres from old newspapers and magazines. [50] If recovered paper is pulped and de-inked, additional components such as inks and adhesives are removed, leaving only the recycled fibres for further use. However, recycling is known to induce morphological and chemical changes in recovered fibres, such as fibre hornification, hydroscopic properties, fibre charging and flexibility. [51] The additives in addition to reject fibres from the de-inking process remain in the sludge generated by the process, which is typically used in energy production or landfilled.

Liquid packaging boards or cartons used for beverage and food packaging constitutes typically of multilayer materials. For example, in milk and juice packaging, paperboard typically consist of two- or three-layer board of virgin fibres, including both bleached chemical pulp as well as mechanical or chemi-thermomechanical pulp. The board is often treated with hydrophobic sizing additives and coated with PE on both sides, or aluminium on internal layer of the package. [50] In LDPE matrix, multilayer cartons have been shown to preserve or improve composite performance with the adequate addition of coupling agent to the system. [52]

4 WOOD-BASED FIBRES AS COMPOSITE REINFORCEMENT

4.1 Parameters affecting reinforcing capability of wood fibres

The key parameters for fibres to be able to reinforce a composite material are: 1) aspect ratio; 2) fibre physical properties; 3) interfacial bond between the fibre and the polymer matrix; 4) dispersion and distribution of the fibres in polymer matrix; and 5) fibre orientation, concentration and void fraction. These parameters are considered in the next paragraphs, with emphasis on wood fibres as biocomposite reinforcement.

4.1.1 Aspect ratio

For effective strengthening and stiffening of a composite material, the reinforcing fibre needs to have a length longer than the critical fibre length. [2] The critical fibre length l_c is defined by fibre diameter d, fibre tensile strength σ_f^* and fibre-matrix bond strength τ_c (or the shear yield strength of the matrix, if it is smaller), according to

$$l_c = \frac{\sigma_f^* \, \mathrm{d}}{2\tau_c}$$

From the equation, it can be seen that critical fibre length is proportional to the fibre diameter. In other words, as fibre diameter is reduced, the shorter the fibre can be while still achieving the critical fibre length needed for efficient reinforcement. Therefore, one of the most important parameters affecting the reinforcement capability of fibre in a composite matrix is its aspect ratio: fibre length divided by fibre diameter (or fibre width). If reinforcing fibres have dimensions significantly lower critical fibre length or aspect ratio, proper stress transfer does not occur, thus the reinforcement capability of the fibres remains low. [2]

In case of wood-based lignocellulosic fibres, native fibres are always discontinuous with relatively low fibre length, thus significant improvements especially in impact strength cannot be expected [53]. For *P. radiata* pine, the critical fibre length in polypropylene matrix has been estimated to be about 0,8 mm, consistent with model calculations.[54] On the other hand, critical fibre length has been found to vary depending on fibre and matrix type, fibre treatment and fibre content [55], as the equation takes also into account the fibre-matrix adhesion and fibre strength characteristics. If not fractioned, pulp fibre dimensions are always a distribution of various lengths, including fines, of which properties differ significantly from the other fibre fractions. [42]

The use of higher aspect ratio fibres instead of e.g. wood flour has been shown to improve mechanical properties in several studies. [56–58] On the other hand, fibre length reduction during thermoplastic melt processing has been determined to be higher with longer fibres. [59] In any case, compounding and injection moulding processes inevitably contribute to fibre length reduction. [60] Processing of moist BSKP fibres resulted in decreased fibre attrition during processing presumably due to decreased shear forces caused by plasticising effect of water. [61] As critical fibre length after melt processing is hard to achieve, fibre length is not the most significant factor in improving mechanical properties of natural fibre composites. [54]

4.1.2 Fibre physical properties

Fibre physical properties include fibre strength, stiffness and density, which all vary significantly depending on the fibre source. [62] In case of pulp fibres, fibre properties are also influenced, e.g., by pulping and bleaching process. [42] The differences between mechanical and chemical pulps are presented in Table 3. When residual lignin is removed by bleaching of chemical kraft pulp fibres, fibres can swell more freely, which increases their flexibility and pliability. However, the chemicals also weaken the fibres by decreasing cellulose molecular weight of the fibres [63], leading to higher refinability of bleached fibres [45]. Commercial batch cooked pulps before oxygen delignification stage (i.e. bleaching) have been reported to obtain better fibre stiffness and strength than after bleaching. [64] In PLA composites, unbleached fibres have been shown to provide higher mechanical properties compared to bleached fibres due to higher intrinsic strength of the fibres. [65] When

pulp fibres are recycled, chemical fibres have been reported to hornificate and loose their originally high bonding ability, while mechanical fibres do not deteriorate, showing good recyclability characteristics. [51] Overall, production of paper causes mechanical fibre damages, such as fibre attrition resulting in higher fines content of recycled fibres compared to virgin ones.

Table 3. Some properties of mechanical and chemical pulps [42]

Property	Mechanical pulps	Chemical pulps
Structure	Stiff, coarse, straight	Slender, curly, kinky
Shape	Short and wide	Long and narrow
Bending stiffness	High	Low
Fines content	High	Low
Amount of lignin	High	Low
Amount of hemicelluloses	High	Low
Specific surface area	Large	Small

4.1.3 Interfacial adhesion

When a discontinuous fibre reinforced composite with strong fibre-matrix adhesion is placed under an external load, the shear action of the matrix generates an interfacial shear stress or load to the fibres, which then deforms elastically. [66] The maximum fibre load is achieved only at the axial centre of the fibre. [2] Higher fibre-matrix interaction has been shown to lead to higher axial stress. [67] Coupling is often needed to generate covalent bonding or specific interactions between hydrophobic polymers and hydrophilic lignocellulosic fibres. Especially in wood fibre reinforced PP and PE composites, coupling is needed due to high polarity difference. The use of maleic anhydride (MAH) as an interfacial adhesion promoter in wood flour or fibre reinforced PP and PE composites is a well-established and effective method to improve adhesion and consequently, mechanical properties of the composites. [68,69] Figure 6 shows the effect of compatibilisation in pulp fibre reinforced PP composites, with clear gaps in fibre-matrix interface without maleic anhydride grafted polypropylene (MAPP) addition.

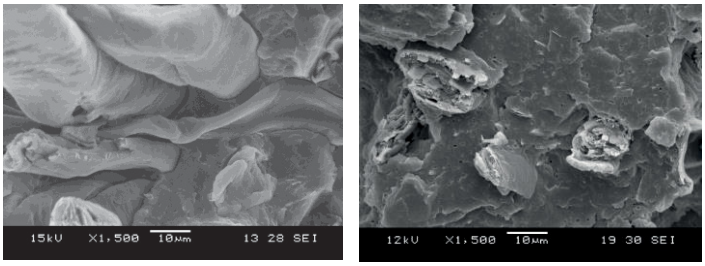


Figure 6. Bleached kraft pulp reinforced PP composites without (left) and with (right) maleic anhydride compatibilisation. Picture by Author from non-published sources.

In case of PLA, its interfacial adhesion with lignocellulosic fibres is naturally relatively strong due to specific interactions between polyester matrix and cellulose.[70–72] However, several studies have been reported to further improve the coupling between lignocellulosic fibres and PLA, e.g., by utilisation of external additives [73], lignin [74], fibre acetylation [75], as well as maleic anhydride [76], silane [77] and alkali [78] treatments. Within external additives, epoxidated linseed oil has been reported to act as reactive plasticiser and a combined plasticiser-coupling agent in bleached softwood kraft pulp reinforced PLA composites.[79] External additives can also be used as lubricants for compacted wood based fibres to improve fibre dispersion and reduce fibre attrition during processing. [80] Generally, external additives are advantageous over often complex fibre chemical treatments, as they can be introduced e.g. in fibre compacting stage in a simple and affordable way. [81]

In addition to various treatments, also the residual lignin and fibre bleaching can affect the interaction between polymer and fibres, and therefore also overall composite performance. Hydroxen peroxide bleaching of oil palm empty fruit bunch improved mechanical properties of PLA by enhancing the fibre-matrix interfacial adhesion and increasing the crystallinity of the fibre by removal of lignin and hemicelluloses, but the fibres were not pulped or results reflected to chemical composition of the fibres. [82] In PP composites, the removal of lignin and hemicelluloses from kraft pulp improved fibre-matrix interfacial adhesion and increased crystallinity of the fibres, which led to slight improvement of mechanical performance of the composites. [83] In low-density polyethylene composites, unbleached batch cooked pulps has provided improved impact strength compared to bleached fibres. [64]

4.1.4 Dispersion and distribution

Good fibre dispersion is essential to obtain unrestricted interfacial adhesion between matrix polymer and fibres. Without fibre-matrix contact, the stress transfer from polymer matrix to fibre is not possible, i.e. the fibre-fibre surfaces are unable to act as reinforcement, but more as weak spots for crack propagation. If the requirement is to maintain the fibre length of pulp fibres, fibres need to be in a compacted form to be able to feed them into twin-screw extruder. Thus, reaching both good fibre dispersion and length can be contradictory: while dispersion of pelletised cellulose fibres can be challenging, increasing shear energy improves dispersion but leads to higher fibre breakage. [60] Uniform fibre distribution provides same properties for the material throughout the product without possibility of local crack propagation or uneven stress transfer. The differences of fibre dispersion and distribution are illustrated in Figure 7.

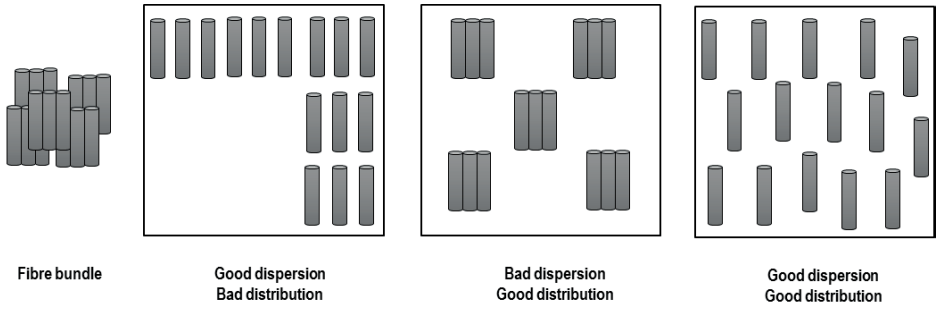


Figure 7. Fibre dispersion and distribution in a polymer matrix

The dispersion and distribution of fibres is highly affected by the melt processing conditions. Dispersion can be improved by screw type and design [59], but also the selected polymer and the corresponding processing parameters affect the dispersion properties. The dispersion is attributed to shear forces establishing during melt processing. Shear forces are dependent on the rheological properties of the polymer melt, which can be controlled by e.g. polymer selection [84], filler size [85] and level [86], fibre characteristics [87], plasticiser content [88], as well as compounding temperature [89] and set-up [59].

4.1.5 Fibre orientation, concentration and porosity

Fibre orientation and concentration significantly affect the overall performance of composite materials. In continuous fibre composites, highly oriented fibres provide maximum reinforcement in the longitudinal direction, but reinforcing effect is close to zero in transverse direction. [2] However, in short lignocellulosic fibre reinforced composites produced by melt compounding and injection moulding processes, fibre orientation is more random, with some alignment in melt flow direction. [90,91] Randomly and uniformly distributed fibres provide more uniform mechanical properties to the composite in all directions, but reinforcement efficiency is one fifth of aligned fibre reinforcement. [2] Pulp fibres have been reported to provide more isotropic reinforcement compared to glass fibres, improving the overall mechanical performance of studied PP composites. [92]

Regarding fibre concentration, strength and stiffness of composite material typically increases with increasing fibre content. [53] However, reinforcement capability is dependent on retaining sufficient fibre-matrix interfacial adhesion, thus there exists a maximum obtainable fibre volume fraction that determines the transition point at which the composite stiffness is as high as possible. [93] Stiffness has been reported to increase with fibre contents up to 55-65 weight-percent (wt-%). [55] In wood flour filled composites including various biopolymer matrixes, fibre content of 40 wt-% was reported as an upper limit for beneficial overall composite performance. [84] For compression moulded PLA composites reinforced with unbleached fibres, maximum stiffness was reached at 50 wt-% fibre content. [65]

The reasons behind porosity found in lignocellulosic fibre composites is summarised by Madsen et al. [93] to five main factors:

1) Natural luminal cavities in plant fibres
2) Varying and complex surface chemistry of plant fibres, which affects the fibre/matrix adhesion
3) Irregular morphology of plant-based fibres, complicating the polymer impregnation
4) Low packing ability of plant fibres, limiting the maximum obtainable fibre volume fraction
5) Conventional processing methods which are not tailored for natural fibre composite production.

Thus, porosity in natural fibre composites is unavoidable. In general, porosity of natural fibre composites has been reported to increase with increasing fibre weight fractions. [94] On the other hand, Madsen et al. suggest that rather than using fibre weight fraction values, they should be converted into fibre volume fractions, which requires data on fibre and matrix densities as well as composite porosity. [93] In PLA composites, a correlation between stiffness and fibre volume fraction has been demonstrated with relatively high porosity which increases with fibre loading. [95] Fibre/fibre interaction was speculated to be one of the key elements in addition to fibre-matrix interphase and porosity to define the stiffness and strength of the produced composites.

4.2 Wood fibre based biocomposites

As wood-based fibres, especially after pulping, obtain fibrous structure with sufficient aspect ratio, their use in biocomposite reinforcement has shown potential both in research and commercial applications. This Chapter concentrates on wood fibre based biocomposites based on PLA matrix, including extrusion foamed biocomposite structures as a new potential light-weight application area.

4.2.1 Wood fibres as PLA reinforcement

In general, several natural fibre types have been used as PLA reinforcement, including flax, cordenka, hemp, jute, bamboo and kenaf fibres. [96–100], but also wood based fibres have received relatively high attention.

Within wood fibres, several wood fibre types in PLA-based biocomposites have been studied, including bleached kraft pulp, chemi-mechanical pulp, thermomechanical pulp, recycled fibres, microcrystalline cellulose, nanocellulose and wood flour. [61,75,79,101–106] While the use of wood flour or pulverised/ground pulp fibres with low initial fibre length decrease the strength of PLA composites [102,107–109], untreated bleached softwood kraft pulp has been reported to improve tensile properties [72,73]. However, fibre contents above 30 wt-% have shown reduced performance due to lack of interfacial adhesion [73]. Introduction of

BSKP fibres also showed improvement in crystallisation rate of PLA with decreased thermal stability (degradation) compared to neat PLA. [110] Utilisation of moist BSKP fibres resulted in lower fibre attrition during processing and less energy-intensive processing without significant effect on mechanical properties. [61] Addition of cellulose fibres has also been reported to increase the biodegradation rate of PLA. [111]

In addition to virgin fibres, the use of recycled wood fibres has also been studied. Recycled newspaper with and without talc addition has been reported to provide improved properties to PLA. [104,112] Mechanical performance was shown to be even comparable to glass fibre reinforced PP composites. [113] Apart from injection moulding applications, recycled fibres such as pulp and paper solid sludge and reject fibres have also showed potential in compression moulded PLA based biocomposites. [114,115]

4.2.2 Wood fibres in extrusion foamed biocomposite structures

While solid biocomposites are feasible for several applications, they do exhibit some shortcomings, such as high density and poor mechanical workability. Foaming can provide solutions for these shortcomings, especially when suitable foaming technique and applicable cellular structure are achieved. [76],[77] By density reduction, foaming can offer totally new application areas for biocomposite materials, such as packaging, construction and light-weight components for automotive sector. In addition, small density decrease e.g. in decking products could result in densities comparable to wood, providing more resource efficient solutions.

In thermoplastic polymer foaming, a blowing agent is introduced to polymer melt to induce foam formation, followed by cooling to solidify and stabilise the foam. [118] Thermoplastic low density foams are typically produced by extrusion foaming using a physical blowing agent, such as carbon dioxide, nitrogen or isobutane, that is diffused and dissolved into a molten polymer. By bubble nucleation and fast change in thermodynamic stability when entering the die (pressure and temperature drop), phase separation occurs, and bubbles grow and stabilise. [119] The basis for the foaming phenomena is illustrated in Figure 8. The process is especially sensitive to correct processing parameters in the die zone, requiring correct die pressure and polymer melt temperature for the bubbles to be able to grow and keep their shape

without cell collapse or rupture. Through successful foaming, density of the material is inevitably reduced. By decreasing weight, the ecological footprint of the material can be decreased by contributing to material, energy and cost savings. Cellular structure also provides material characteristics such as thermal insulation properties, and material properties can be tailored by designing foams, e.g., with varying densities, cell sizes or open vs. closed cell structures. [120]

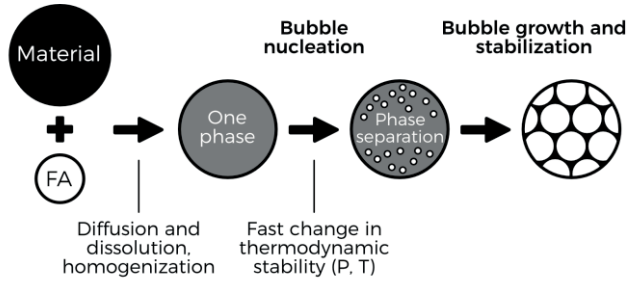


Figure 8. Foaming phenomena in thermoplastic polymer foaming. FA = foaming agent. Picture by Teijo Rokkonen, VTT

While biopolymer foams have gained a lot of interest in the literature [121–126] and also some commercial applications already exist [127], extrusion foaming of wood based biocomposites has been paid less attention. Most of the research has been conducted using either wood flour or wood fibres as reinforcement in fossil-based plastics, such as polypropylene [128], high-density polyethylene [129], polystyrene [130] or polyvinyl chloride (PVC) [116]. Only a limited number of studies have concentrated on foaming of cellulose or pulp fibre reinforced PLA composites [131–136], from which only few cover extrusion foamed structures using physical blowing agents. In general, it has been concluded that cellulosic fibres promote cell nucleation in PLA foams. [132,135,136] In addition, it was reported that addition of 20 wt-% of cellulose fibres supressed expandability and increased cell density of PLA. [131]

While wood fibre reinforced biocomposites show potential in foamed structures, they possess certain challenges in foaming process needing special attention. Especially the moisture in wood can lead to unwanted transactions. Wood fibres can contain water in three different forms: free, bound and chemical. Free, liquid water can be easily removed by drying. If free water is not removed, it remains as a separate

phase during foaming process and evaporates after the pressure is released. High amounts of water can lead to high cell size distribution and cause bubble rupture, which can lead to significant blowing agent loss. Thus, careful drying with minimum moisture content is required to achieve optimal cell structures. [130,137,138] Compared to free water, bound water is more challenging as it is bonded to the structure by intermolecular forces. If wood fibres are exposed to prolonged heating during extrusion foaming, bonded water can evaporate as moisture and other volatile organic compounds and extractives through chemical decomposition. [130,139] As bleached kraft pulp fibres contain less extractives than mechanical pulps, lower emission of volatiles during processing should be obtained, leading to less deteriorated cell morphologies.

5 OBJECTIVES OF THE STUDY

The main target of the study was to increase the understanding of the effect of fibre morphologies on reinforcement of wood fibre based PLA biocomposites. The objective was to gain knowledge of how fibre selection, several fibre pre-treatments and melt processing influence the material end-properties. Attention was paid especially to retained fibre dimensions after melt processing, fibre dispersion and fibre-matrix adhesion. In general, the objective was to maintain the fibre length in the initial stage as long as possible, and compare various fibre types, including recycled fibres, as PLA reinforcement. In addition, the objective was to introduce kraft pulp fibres in foamed PLA structures and evaluate the effect of fibre addition on foamability of PLA.

The *research questions* are the following:

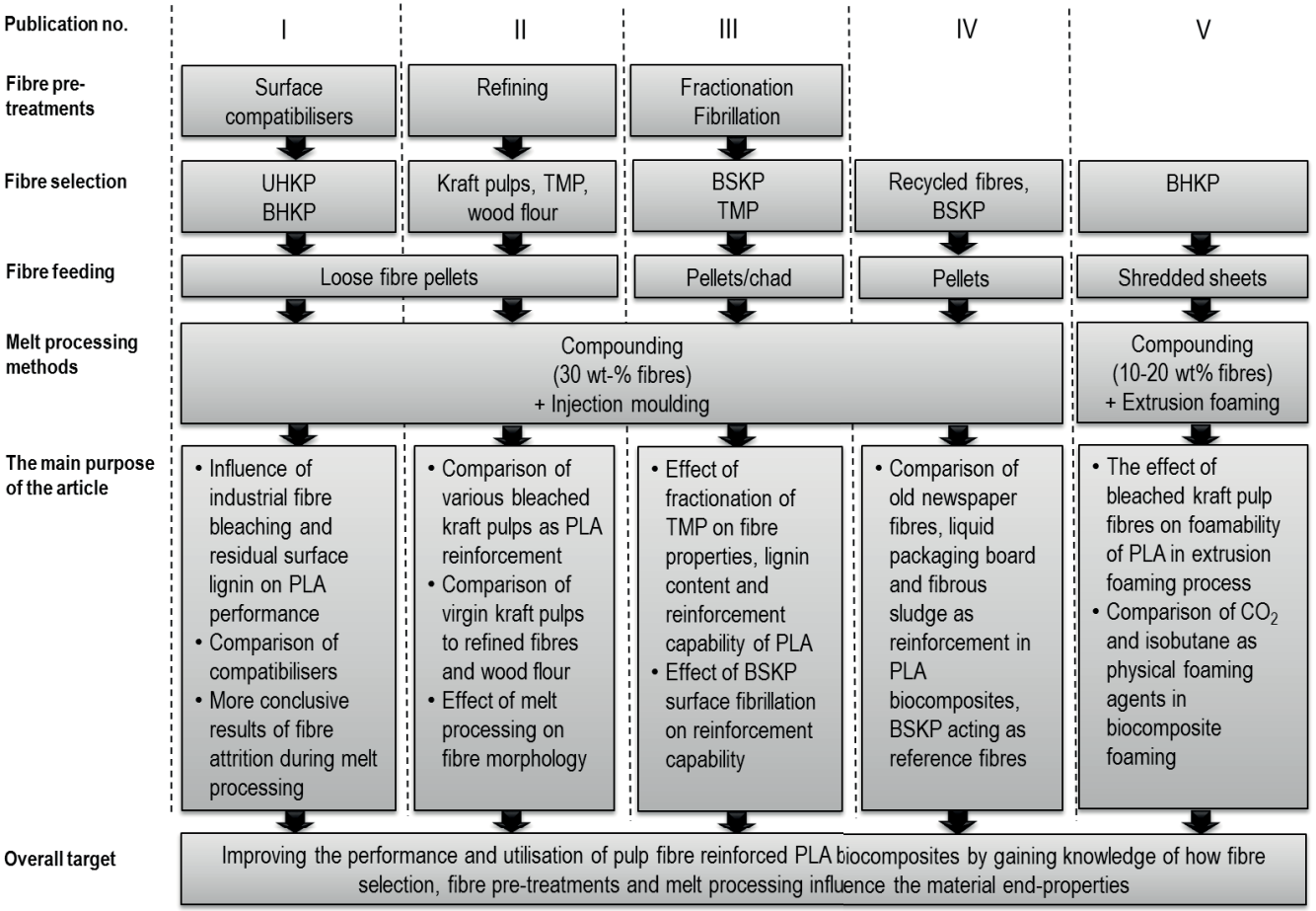
1. What is the effect of melt processing on fibre morphologies of various pulp fibre types used as PLA reinforcement?

2. What is the reinforcing effect of various pulp fibre types in PLA and is there a correlation between the fibre morphology and biocomposite performance?

3. Does fibre surface treatments, such as industrial bleaching, surface compatibilisation or physical treatments affect the reinforcement capability of wood-based fibres?

4. How does pulp fibre reinforcement influence foamability of PLA in extrusion foaming?

By answering these questions, the ultimate target is to improve the performance and utilisation of wood fibre reinforced PLA biocomposites and broaden their use in commercial applications, as well as open new business opportunities for these materials.


Publication no.
I
II
III
IV
V
Fibre pre-treatments
Surface compatibilisers
Refining
Fractionation Fibrillation
Fibre selection
UHKP BHKP
Kraft pulps, TMP, wood flour
BSKP TMP
Recycled fibres, BSKP
BHKP
Fibre feeding
Loose fibre pellets
Pellets/chad
Pellets
Shredded sheets
Melt processing methods
Compounding (30 wt-% fibres) + Injection moulding
Compounding (10-20 wt% fibres) + Extrusion foaming
The main purpose of the article
• Influence of industrial fibre bleaching and residual surface lignin on PLA performance
• Comparison of compatibilisers
• More conclusive results of fibre attrition during melt processing
• Comparison of various bleached kraft pulps as PLA reinforcement
• Comparison of virgin kraft pulps to refined fibres and wood flour
• Effect of melt processing on fibre morphology
• Effect of fractionation of TMP on fibre properties, lignin content and reinforcement capability of PLA
• Effect of BSKP surface fibrillation on reinforcement capability
• Comparison of old newspaper fibres, liquid packaging board and fibrous sludge as reinforcement in PLA biocomposites, BSKP acting as reference fibres
• The effect of bleached kraft pulp fibres on foamability of PLA in extrusion foaming process
• Comparison of CO_2 and isobutane as physical foaming agents in biocomposite foaming
Overall target
Improving the performance and utilisation of pulp fibre reinforced PLA biocomposites by gaining knowledge of how fibre selection, fibre pre-treatments and melt processing influence the material end-properties

6 EXPERIMENTAL

6.1 Materials

The matrix polymer for all the produced materials was poly(lactid acid) purchased from NatureWorks LLC (U.S.A). The used PLA grades in different publications are seen in Table 4.

Table 4. PLA grades used in the dissertation

Pub. no	Grade	Purpose	MFR, g/10min (210ºC, 2.16kg)	Tensile yield strength (MPa)	Tensile elongation (%)
I	Ingeo™ 3052D	Injection moulding	14	62	3.5
II, III	Ingeo™ 3051D	Injection moulding	10-36	48	2.5
III	Ingeo™ 3001D	Injection moulding	14	62	3.5
V	Ingeo™ 8052D	Extrusion foaming	14	62	3.5

The study covered various fibre types from pulp and papermaking processes. Fibres utilised in the study are listed in Table 5.

Table 5. Fibre types used in the study

Acronym	Fibre	Provider
UHKP	Unbleached hardwood kraft pulp (birch)	UPM Kymmene Oyj
BHKP	Chemically bleached hardwood kraft pulp (birch)	UPM Kymmene Oyj
BHKP-e	Chemically bleached softwood kraft pulp (eucalyptus)	UPM Kymmene Oyj
BSKP	Chemically bleached softwood kraft pulp (spruce)	UPM Kymmene Oyj
BSKP-r	Refined Chemically bleached softwood kraft pulp (spruce)	UPM Kymmene Oyj/Pallmann
TMP	Thermomechanical, peroxide-bleached pulp (spruce)	UPM Kymmene Oyj
WF	Wood flour, sawmill side stream (pine/spruce)	Local sawmill
ONP	Old newspaper containing recycled fibres and fillers (<15 wt%)	Collected and pulped by VTT
LPB	Liquid packaging board without PE-coating. Top and bottom plies made of solid bleached sulfate pulps and the middle ply mainly of mechanical pulp like CTMP but containing also some BSKP. The board is sized with hydrophobic and/or wet strength sizes to reduce liquid absorption and improve wet strength.	Stora Enso Oyj
FS	Fibrous sludge containing 60% inorganic material, about 40% organic material and material from the flotation deinking, the screening rejects of the recycling process, and other paper mill reject streams.	UPM Kymmene Oyj, Kaipola recycled pulp mill

For the compatibilisation studies (Publication I), various selected additives were trialled. The used additives are listed in Table 6.

Table 6. Used compatibilisers

Trade name and producer	Acronym	Functionality / description	Main application defined by producer
Vikoflex 7190 (Arkema)	ELO	Epoxidised linseed oil; Primary, polymeric type, plasticiser-stabiliser	Food contact applications, PVC homopolymer and copolymer plasticisation and stabilisation
Vinnex 2525 (Wacker)	PVA	Poly(vinyl acetate) based binder	Compostable binder for biopolymer systems, PLA processing improvement modifier
Dynasylan GLYEO (Evonik)	EPX	Bifunctional organosilane with epoxide and triethoxysilyl group	Coupling agent, cobinder/copolymer, crosslinking agent
Geniosil XB 502 (Wacker)	SIL	Silicon reinforced polyether-based silane-terminated polymer (alpha-silane technology)	Reactive binder for adhesives, potting compounds and coatings, used especially for bonding wood

6.2 Fibre treatments

Fibre pre-treatments

Part of the publications I, II and III concentrated on various pre-treatments of pulp fibres and their effect on performance of the obtained biocomposites. In publication I, the UHKP and BHKP fibre were obtained in never-dried from. The unbleached fibres were collected from the pulp line after acidification, and the bleached fibres were taken from the same batch after the bleaching process. Both fibres were delivered to VTT having dry solid content (d.s.c.) of 10%. Due to high alkalinity of the UHKP fibres, the fibres were washed by diluting the pulp to d.s.c. of 4% and the thickening it to 10%, repeating the sequence 5 times with diffusion time of 10 minutes in between. After washing, the batches were mixed together, centrifuged to 35% d.s.c., homogenised, and fractioned by removing large fibre chips from the batch.

Surface compatibilisation. The introduction of liquid surface additives (ELO, EPX and SIL) were performed by breaking up the fibre cakes by using a Forberg mixer and spraying the additives onto the fibres during mixing to concentration of

5 wt-% with respect to fibres. Vinnex (PVA), as a solid, granulate form additive, was introduced in the compounding stage.

Refining. In publication II, BSKP fibres were refined in dry stage in Pallmann Machinenfabrik GmbH & Co. KG (Germany) (referred as BSKP-r), providing an optional method for fibre feeding, as well as acting as a comparison to virgin BSKP fibres.

Fractionation. Fractionation of TMP (Publication III) was performed using Metso FS-03 laboratory screen type sorter in nine sorting steps into short and long fractions, unfractioned TMP acting as a reference.

Surface fibrillation. In publication III, surface fibrillation (surface refining) of BSKP was performed by using Escher Wyss laboratory refiner LR1 equipment. The fibres were refined to two different levels with refining energies of 120 or 200 kWh/t.

Fibre compacting, shredding or cutting

The main goal of fibre compacting was to enable adequate fibre feeding into compounder together with securing good fibre dispersion and distribution in compounding stage. If not stated otherwise, all pulp fibres were compacted, shredded or chad to decent feeding form. In publication I, UHKP and BHKP fibres received as never-dried form were compacted in d.s.c. of 35% to loose fibre pellets using a VTT patented E-compactor. After compacting, the pellets were gently broken down by running them through a feeder with double-screws to enable sufficient fibre dispersion. In the case of other publications (II-V), the fibres were received from the pulp supplier in a once-dried form. For pelletising, pulp sheets were rewetted and pelletised to loose fibre pellets using planar matrix pelletising machine (Amandus-Kahl). TMP fibre chads after fibre fractionation (Publication III) were prepared by preparing thick fibre sheets and cutting them into chads using a paper shredder. For shredding (Publication V), once-dried pulp sheets were cut to smaller pieces and shredded into small chips using Rapid low-speed granulator with disc screen. The various fibre forms used in the study are shown in Figure 9.

Figure 9. Treated fibres for compounding process: pelletised (left); chad (middle); shredded (right)

6.3 Processing

Injection moulding experiments

For injection moulding purposes (Publications I-IV), pulp fibres were compounded with PLA to fibre content of 30 wt-%. In case of surface additives (Publication I), the additive content was 1.5 wt-%, substituting same amount of PLA in the compound. Compounding was performed using Berstorff co-rotating twin-screw extruder either with ZE25x48D (Publication I, IV) or ZE25x33D (Publication II, III) screw profiles. Fibres were fed through gravimetric feeders. The detailed processing data are shown in Table 7. After compounding, the materials, including reference samples from neat polymers, were injection moulded into ISO 3167 tensile test specimen using a cold mould with an Engel ES 200/50 HL injection moulding machine. Before testing, tensile test specimen were stored in standard conditions (23°C, 50% relative humidity) for at least 5 days before testing.

Table 7. Processing parameters used in the experiments

Pub. No	Screw profile	Temp. profile	Screw speed	Fibre moisture
I	ZE25x48D	40 → 190	200 rpm	90%
II	ZE25x33D	60 → 190	200 rpm	dry
III	ZE25x33D	60 → 190	200 rpm	dry
IV	ZE25x48D	60 → 190	200 rpm	dry

Extrusion foaming experiments

For extrusion foaming experiments (Publication V), PLA was compounded with 10 and 20 wt-% of BHKP fibres using Berstorff ZE25x48D twin-screw extruder. In addition to pulp fibres, 0.7 wt-% of Joncryl 4368-CS (BASF, Germany) was added

as a chain extender (CE) to enable high-quality foaming. The chain extender was added from the last feeding zone to minimise any side reactions in the compounding stage. The chain extender was fed as a 30% pre-produced masterbatch. PLA and the masterbatch were dried at 75 °C in vacuum overnight and the fibres were dried at 50 °C overnight. The temperature profile for the compounding were 40-195-190-185-180-180-180-175-175-175-175°C, with die temperature of 200°C. The extruded materials were cooled down using a water bath.

The extrusion foaming of the produced compounds was performed with a Brabender Plastograph EC Plus with 19 mm single screw, melt pump and melt cooler. Carbon dioxide and isobutane were used as blowing agents in 5 wt-% content using Teledyne Isco Dual pump. To ensure good nucleation, 0.1 wt-% of Finntalc M05SL talc was added to the compounds by bag mixing. All the materials were dried at 60°C overnight before foaming. The detailed extrusion foaming set-up and parameters is described in Publication V.

6.4 Characterisation

Chemical composition of the fibres

Chemical composition of the fibres (Publication I) were analysed based on modified NREL method. After Soxhlet extraction and determination of extractives, the resulting monosaccharides were determined using high-performance anion-exchange chromatography (HPAEC) with pulse amperometric detection. The polysaccharide content in the samples was calculated from the corresponding monosaccharides using an anhydro correction of 0.88 for pentoses and 0.9 for hexoses. Klason lignin content i.e. the insoluble residue from the hydrolysis was analysed gravimetrically. Acid soluble lignin was determined from the hydrolysate based on UV at 215 and 280 nm using equation described by Goldschmid. Ash content was measured gravimetrically after burning the samples at 550 °C for 23 h.

Surface chemical composition of the fibres

The chemical composition of fibres (Publication I) were analysed using and X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra spectrometer. The analyses

were performed from loose fibres, using pure cellulose filter paper as in-situ reference.

Fibre dimension analyses

Fibre dimensions were analysed using automated fibre analyser L&W STFI FiberMaster equipment. Dry fibres were dispersed in water, and the fibre dimensions were analysed by image analysis method by determining the length, width, aspect ratio and fines proportion of the sample. The fines content of the measurements equalled fibres with dimensions lower than 0.2 mm. To measure processed fibres, PLA matrix was dissolved from biocomposite samples using chloroform.

Tensile testing

All tensile tests were performed using modified ISO 527 standard with 5 mm/min cross-head speed. The used tensile test equipment was Instron 4505 Universal Tensile Tester with an Instron 2665 Series High Resolution Digital Automatic Extensometer. The results were averages of five reference samples.

Impact strength tests

Impact strength tests were based on Charpy impact test according to standard ISO 179. Tests were performed using a Charpy Ceast Resil 5.5 Impact Strength Machine on unnotched specimens using 2 J pendulum. The impact strength was calculated based on the impact energy measured by the equipment.

Fibre-matrix adhesion

Adhesion between PLA and fibres were detected using A JEOL JSM-6360LV scanning electron microscope (SEM). For sample preparation, biocomposite samples were fractured using liquid nitrogen, gold coated with Bal-Tec Balzers SCD050 sputter coater. The fracture surfaces of the prepared samples were investigated to evaluate the adhesion between matrix polymer and applied fibres.

Fibre dispersion

Fibre dispersion in PLA was investigated by using microscopic means. Thin microtome samples were analysed using a Wild Heerbrugg M5A stereo microscope. For macroscopic evaluation, conventional digital camera was used to take comparable pictures of the samples.

Density measurements

Densities of the extrusion foamed samples (Publication V) were analysed using a liquid submersion technique and weighting the corresponding samples. The measurements were performed to at least three reference samples.

7 RESULTS AND DISCUSSION

This Chapter presents the most important results of the studies presented in the attached five publications. First, the effect of melt processing on fibre morphologies of various fibre types are addressed. After that, the effect of fibre surface treatments and fibre selection on biocomposite performance are discussed. Lastly, extrusion foaming of wood fibre reinforced PLA biocomposites is evaluated in means of fibre addition and blowing agent type.

7.1 Effect of melt processing on fibre morphologies

Natural fibres, including pulp fibres, are sensitive to high temperatures and shear forces applied during thermoplastic processing methods. Thus, pulp fibre length is inevitably reduced by compounding process.[80,140] The effect of fibre compacting and melt processing on pulp fibre breakage in PLA matrix using various pulp fibre types was studied in Publications I-III. The aim was to try to maintain the reinforcement capability of lignocellulosic fibres by using them in their initial fibre length, i.e. without fibre refining/grinding. To be able to feed long pulp fibres into a twin-screw extruder, the fibres need to be in a compacted stage. On the other hand, once-dried pulp sheets could be re-pulped to obtain more loose fibres for better fibre dispersion. Publications I and III showed that well executed pelletising process maintains fibre length with both hardwood and softwood pulps (Figure 10.). Addition of ELO gives a slight protective effect to the fibres during pelletising.

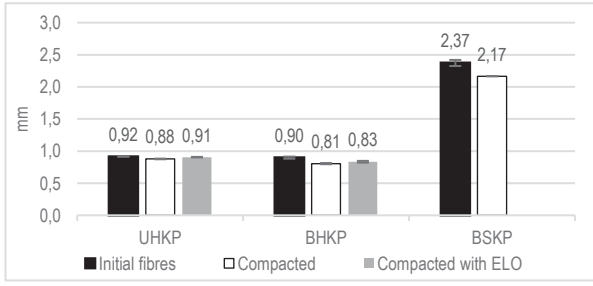


Figure 10. Effect of compacting on fibre average length (combined results from Publications I & III)

However, exposing pulp fibres to harsh processing conditions with high temperatures and shear forces leads to evident fibre attrition and cutting. In case of pulp fibres from different sources with varying initial fibre lengths (Publication II), fibre lengths are reduced to the same level due to high melt viscosity of PLA, independent of the initial fibre source (Figure 11.), also observed by by Ariño and Boldizar [59]. The amount of fines (fibres under 0,2 mm) is simultaneously increased.

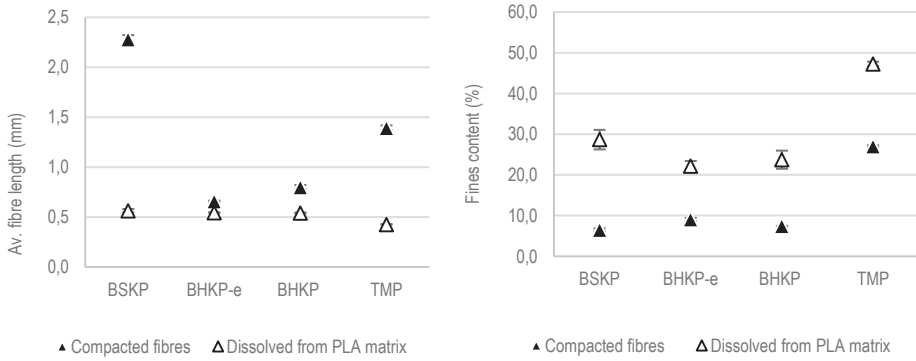


Figure 11. Effect of processing on fibre length characteristics of various pulp fibres in PLA 3051D matrix, compounded with screw length 25x33D

Comparing unbleached and industrially bleached hardwood kraft pulp fibres, bleached fibres show a higher degree of fines generation and fibre length reduction, as seen from Figure 12. This is probably due to the fact that bleached fibres have higher refinability [45], leading to increased attrition during processing. As an oil-based additive, the addition of ELO reduces fibre attrition of bleached fibres probably by lubricating the fibres and reducing the fibre friction during processing. In unbleached fibres, the effect is not as strong, as fines content is already low, and lignin may have similar effect in reducing fibre friction with less fibre bending/twisting due to stronger fibres.

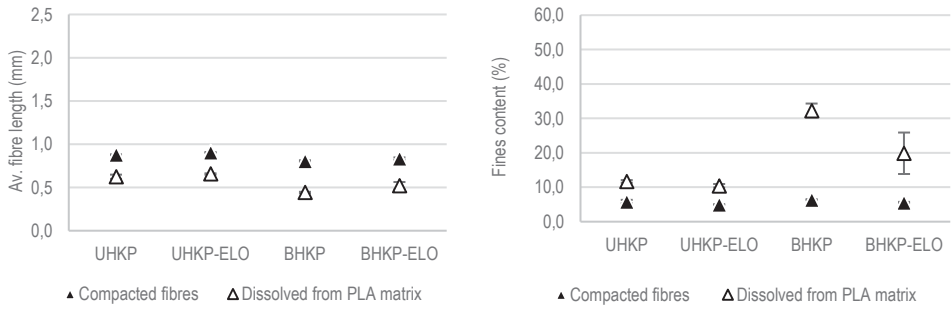


Figure 12. Effect of processing on fibre length characteristics of unbleached and bleached pulp in PLA 3052D matrix, compounded with screw length 25x48D

While the studies reveal the unavoidable loss of fibre length by melt processing, the measurements show that fibre diameters have not decreased (Figure 13.). Therefore, the aspect ratio, being one of the main factors defining the reinforcement capability of the fibres, is affected by: 1) the remaining fibre length after processing, and 2) the initial fibre width of the fibres. However, it should be noted that the fibre width measurements can be somewhat distorted due to remaining polymer on the fibre surfaces (Publication II), and false interpretations of FibreMaster analysis due to fibre collapse to shape by fibre handling and processing.

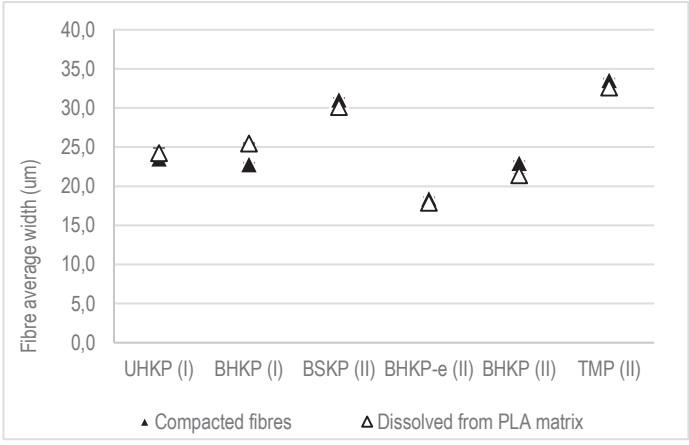


Figure 13. Effect of processing on fibre widths of various fibre types in PLA 3051D (Publication II) and PLA 3052D (Publication I) matrixes.

7.2 Effect of fibre surface treatments on biocomposite performance

7.2.1 Industrial fibre bleaching

As industrial bleaching process is known to effect fibre properties, comparing them to unbleached kraft pulp fibres as PLA reinforcement is an interesting aspect to be studied. In addition, the somewhat higher lignin content of unbleached fibres could provide additional improvements to fibre-matrix adhesion.

As shown in Chapter 7.1, bleaching process did not affect fibre dimensions or fines content of the untreated fibres significantly. The biggest differences can be connected to the change of total lignin contents of the fibres, as bleaching removes residual lignin from the fibre. The XPS measurements supported already reported data that lignin content in fibre surfaces is higher in UHKP fibres. Bleaching also induced more fibre surface fibrillation in the bleached fibres compared to unbleached fibres, as seen from Figure 14. Bleached fibres have also been reported to have increased flexibility and pliability, but potentially at the expense of fibre strength due to shortening of the average cellulose molecular weight.

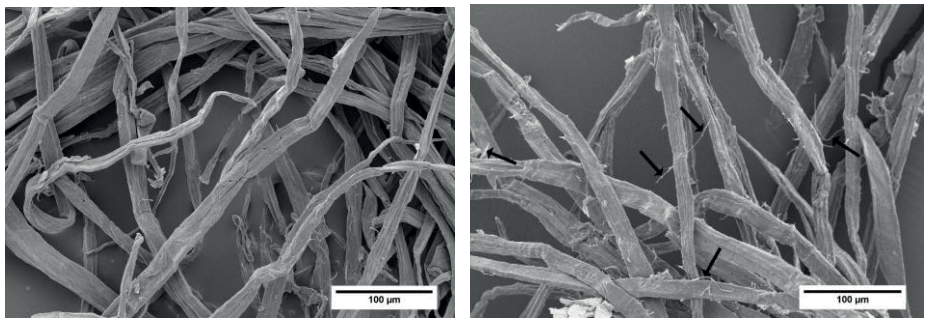


Figure 14. SEM images of unbleached (left) and bleached (right) BHKP fibres

All fibres were evenly dispersed to PLA matrix without significant fibre flocculation or agglomeration, probably due to more intensive mixing as twin-screw extruder with long screw lengths (25x48) were used. Uniform fibre dispersions of the samples were also verified by microscopic imaging. As shown in Figure 15., fibres

were oriented in melt flow direction, as expected by injection moulding process, with some degree of fibre curving or twisting.

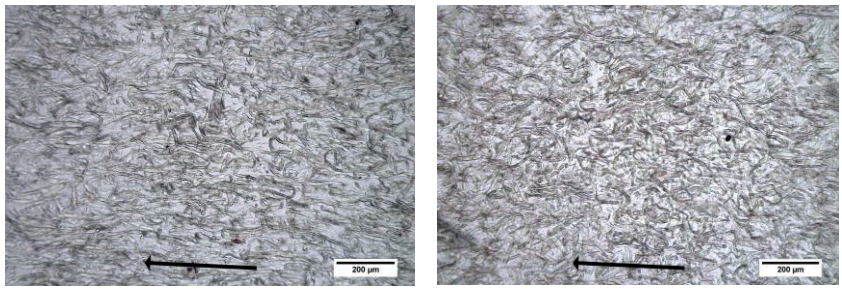


Figure 15. Fibre dispersion and orientation of UHKP (left) and BHKP (right) reinforced PLA composites. Arrow shows melt flow direction of the produced sample.

Regarding composite mechanical performance, it was noticed that the addition of 30 wt-% pulp fibres to PLA increases all characterised physical properties compared with neat PLA, as seen from Figure 16. UHKP fibres provided unexpectedly high physical properties, indicating that there is a high degree of wetting and subsequent interfacial adhesion between PLA and UHKP. As BHKP fibres provided significantly lower mechanical performance in a PLA biocomposite, they might benefit the most from the addition of a compatibilisation agent. The improved performance of UHKP fibres compared to BHKP as composite reinforcement can be related to, e.g., lower fibre attrition during processing, better surface wetting and interfacial bond strength, and higher crystallinity of the produced composite.

Figure 16. Mechanical properties of UHKP and BHKP reinforced PLA composites

7.2.2 Surface compatibilisation

Compatibilisation of cellulose fibre reinforced biocomposites can provide improved properties in certain cases. Therefore, several compatibilisers were compared in terms of their adhesion promotion (Publication I). Of the screened compatibilisation agents, all compatibilisers showed good fibre-matrix interface, apart from Geniosil, which revealed a clear gap in the interface of fibre and matrix polymer, indicating poor fibre-matrix adhesion, with subsequent poor reinforcement of the composites. Comparing mechanical performance, epoxidated linseed oil showed the most consistent property improvement compared to other compatibilisers (Table 8.). ELO has shown to act as reactive compatibiliser in BSKP reinforced PLA composites, with long aliphatic alkyl chain (18 carbons) providing some elasticity to coupling. In addition to reactive compatibilisation, ELO treatment was shown to minimise fibre length reduction during melt processing, thus increasing the reinforcement potential of the fibres. On the other hand, some of the linseed oil might penetrate into the fibre and crosslink internally in the fibre as well, especially in the case of the swollen bleached fibres. Low molecular weight components such as linseed oil and poly(ethylene glycol) (PEG) have been shown to penetrate into the wood cell walls. [141,142] However, for UHKP fibres, ELO treatment had a neutral or slightly negative effect, decreasing slightly the tensile properties. The surface lignin on UHKP fibres might interfere the compatibilising effect of ELO, with a less efficient crosslinking between matrix and fibre. Bleached fibres are less crystalline and there are more available hydrogen for ELO to react with than in unbleached fibres. [143]

Table 8. Mechanical properties of PLA composites with various compatibilisers

Sample	Tensile strength (MPa)	Young's modulus (GPa)	Impact strength (kJ/m^2)	Strain at break (%)
PLA-neat	60,8 ± 0,2	3,58 ± 0,16	16,2 ± 1,2	3,5 ± 0,2
PLA-UBHKP-ref	82,5 ± 0,8	6,26 ± 0,22	32,5 ± 6,5	4,6 ± 0,2
PLA-UHKP-ELO	73,1 ± 0,8	6,43 ± 0,21	33,3 ± 3,1	2,8 ± 0,2
PLA-UHKP-PVA	69,2 ± 0,1	6,37 ± 0,16	30,1 ± 4,5	2,1 ± 0,0
PLA-UHKP-EPX	64,8 ± 0,7	6,23 ± 0,35	34,3 ± 8,3	2,5 ± 0,7
PLA-UHKP-SIL	59,4 ± 0,6	6,16 ± 0,17	24,7 ± 3,1	2,2 ± 0,1
PLA-BHKP-ref	67,0 ± 1,4	6,14 ± 0,48	19,7 ± 3,1	2,1 ± 0,4
PLA-BHKP-ELO	79,3 ± 0,7	6,51 ± 0,19	24,8 ± 2,6	3,8 ± 0,2
PLA-BHKP-PVA	73,6 ± 0,3	6,11 ± 0,23	22,6 ± 3,2	3,6 ± 0,2
PLA-BHKP-EPX	66,3 ± 0,6	6,17 ± 0,15	26,2 ± 6,5	1,7 ± 0,2
PLA-BHKP-SIL	67,4 ± 0,5	6,07 ± 0,27	20,9 ± 2,7	3,9 ± 0,1

7.2.3 Physical treatments

Refining

Successful feeding of short natural fibres to twin-screw extrusion process requires that fibres exist in a compact form to eliminate fluffiness and avoid excess thermal degradation. In addition to compacting the fibres by pelletising, refining of pulp fibres can provide an optional fibre form to ensure adequate fibre feeding in compounding stage. In the study, refining of BSKP fibres in a dry-stage was trialled and compared to virgin, non-refined fibres (Publication II). Additional fractionation of the refined fibres was not conducted.

Refining of BSKP fibres resulted in significant length reduction and increase in fines content (Table 9.). On the other hand, fibre width remained unchanged and fibres were easy to feed in the compounding stage, as expected. Compounding and injection moulding did not significantly affect the fibre aspect ratio of refined fibres, whereas long, pelletised fibres were dramatically shortened. While the difference between aspect ratios of pelletised and refined fibres after melt processing was not high, fines content (fibres under 0.2mm) of the pelletised fibres remained in significantly lower level.

Table 9. Fibre dimensions of virgin and refined BSKP before and after melt processing

Measured properties	Unit	BSKP reference	Dry-refined BSKP	BSKP reference (after melt processing)	Dry-refined BSKP (after melt processing)
Fibre length*	mm	2.28	0.44	0.56	0.36
Fibre width*	µm	31.1	31.0	30.1	29.5
Aspect ratio	-	73	14	19	12
Fines	%	8.6	37.3	28.7	41.0

Mechanical performance of the PLA biocomposites containing 30 wt-% of pelletised or refined BSKP are seen in Table 10. The comparison shows that refining of the fibres resulted in a reduction of all measured properties. In addition, the fibre dispersion was poorer with refined BSKP. Low performance and dispersion is probably due to the fact that fines have large surface area with higher bonding ability. [42] Poor dispersion with reduced low aspect ratio of fines decrease the reinforcing capability and adhesion of the fibres. Removal of fines with narrower fibre length distribution could result in improved reinforcement and thus composite performance.

Table 10. Comparison of mechanical performance of pelletised and refined PLA/BSKP composites

PLA 3051D /BSKP, w-%	Fibre form	Tensile strength, MPa	Elastic modulus, GPa	Impact strength, kJ/m^2
70 / 30	Pellets	74.7 ± 1.6	6.69 ± 0.13	16.1 ± 1.8
70 / 30	Refined	63.8 ± 0.5	4.77 ± 0.11	12.7 ± 1.2

Fractionation

Fractionation of fibres can provide uniform fibre distribution in addition to enabling the use of only long fibres with higher reinforcing potential as composite reinforcement. In the study, TMP was fractionated into short and long fractions, with unfractionated fibres acting as reference (Publication III). After fractionation, the aspect ratio of resulted long fraction was higher than that of short fibre fraction (Table 11.). In addition, fines and lignin content were also affected by fractionation, both being lower in case of long fibre fraction.

Table 11. Fibre dimensions before and after TMP fractionation

Measured properties	Unit	Unfractioned TMP	Short fraction of TMP	Long fraction of TMP
Fibre length*	mm	1.11	0.74	1.23
Fibre width*	µm	34	29	34
Aspect ratio	-	33	26	37
Fines	%	27	47	20
Lignin content	%	26	30	24

As expected, fractionation had a clear effect on the mechanical properties of the produced PLA biocomposites, as shown in Table 12. The use of the short fibre fraction in PLA composites led to reduced mechanical properties, while the long fibre fraction provided improved mechanical performance with improvements in the tensile strength of 7%, impact strength 25%, elastic modulus 7% and elongation 26%. By removing the fines from the TMP, longer, more uniform fibres were obtained, providing better reinforcement capability. As the bonding ability of longer fibres is weaker, it presumably improved the fibre dispersion and thus mechanical performance of the composite. The differences in fibre dispersion is observed already in macroscale, as seen in Figure 17.

Table 12. Mechanical properties of biocomposites including varying TMP fractions

PLA 3001D /TMP, w-%	Fibre fraction	Tensile strength, MPa	Young's modulus, GPa	Impact strength, kJ/m²	Elongation, %
70 / 30	Unfractioned	75.2 ± 1.2	6.19 ± 0.38	14.9 ± 1.9	1.7 ± 0.2
70 / 30	Short	67.7 ± 3.3	5.98 ± 0.32	10.4 ± 2.1	1.5 ± 0.2
70 / 30	Long	80.3 ± 1.2	6.65 ± 0.37	18.7 ± 1.9	2.2 ± 0.3

Figure 17. Produced PLA biocomposites using 30 wt-% of unfractioned (left), short fraction (middle) and long fraction (right) TMP fibres as reinforcement.

Surface fibrillation

Surface fibrillation (surface refining) of pulp fibres increases surface area of the fibres, which could improve fibre-matrix adhesion, and thus also composite properties. Therefore, BSKP fibres were refined at two levels with refining energies of 120 and 200 kWh t-1 (Publication III). The external fibrillation of fibre surfaces through refining can be clearly detected from Figure 18. Fibrillation also increased fines content of the pulp, as seen from Table 13. The increased bonding capacity and fines content of the fibres through surface fibrillation could also be detected from the increased tensile index of the laboratory sheets.

Table 13. Measured fibre properties of unrefined and surface fibrillated (refined) BSKP fibres

Measured properties	Unit	Virgin BSKP	Refining Level 1	Refining Level 2
Specific energy consumption (SEC)	kWh t-1	0	120	200
Fibre length*	mm	2.17	2.10	2.02
Fibre width*	µm	31	31	32
Aspect ratio	-	70	67	63
Fines	%	6.50	9.50	13
Tensile index of paper	Nm g-1	36	59	66

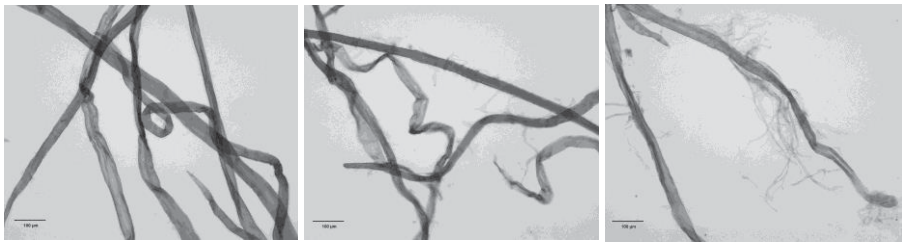


Figure 18. BSKP fibres before refining (left), and after refining level 1 (middle) and level 2 (right)

Even though the surface area of the fibres was clearly increased, refining led to decreased mechanical performance of reinforced PLA composites Table 14. The reduction of mechanical properties is probably due to the increased fines content, which leads to a decreased fibre reinforcement capability of very short fibres as well as decreased fibre dispersion due to the stronger bonding capability of fines.

Table 14. Mechanical properties of PLA composites including 30 wt-% of virgin or surface fibrillated BSKP fibres

PLA 3051D/ BSKP, w-%	Refining	Tensile strength, MPa	Young's modulus, GPa	Impact strength, kJ/m^2	Elongation, %
70 / 30	Unrefined	71.6 ± 0.5	6.38 ± 0.09	16.1 ± 3.7	2.1 ± 0.2
70 / 30	120 kWh t-1	60.4 ± 1.7	6.20 ± 0.04	9.1 ± 1.2	1.2 ± 0.1
70 / 30	200 kWh t-1	61.4 ± 0.3	6.13 ± 0.09	9.4 ± 1.6	1.3 ± 0.0

7.3 Effect of fibre selection on biocomposite performance

Several pulp fibre types are available for biocomposite reinforcement, having varying fibre properties. Comparison of various fibre types as PLA reinforcement provides knowledge on the possible effect of fibre selection on composite performance. Thus, virgin pulp fibres from different sources and pulping methods, as well as utilisation of recycled fibres, were systematically studied and compared in PLA biocomposites (Publications II and IV).

Regarding virgin fibres, comparison was conducted using BSKP, BHKP based on birch and eucalyptus (BHKP-e), TMP fibres as well as wood flour as reinforcement in fibre content of 30 wt-% (Publication II). The dispersion in macro and micro-level, aspect ratio of processed fibres as well as mechanical properties of

the selected fibres as PLA reinforcement were analysed. The outcome of these evaluations are summarised in Figure 19.

As a result, dispersion studies revealed that while BSKP and TMP fibres were uniformly dispersed in PLA matrix, fibre agglomerates after processing were visible with fibres from hardwood sources. The variation in the dispersions might result from more compact pellets derived from hardwood fibres which are harder to disperse, and utilisation of shorter screw design when compared to BHKP-based biocomposites produced in Publication I. Regarding fibre attrition, as explained in Chapter 7.1, melt processing resulted in fibre length reduction of all fibres to a similar fibre length level. Thus, the aspect ratio differences of remaining fibres are derived from fibre width variations of fibres from different sources. Fines content was increased in all composite samples.

While all fibres and fillers typically increase composite stiffness, also strength properties were increased when pulp fibres instead of wood flour were used as reinforcement. In case of wood flour, strength properties were decreased, indicating that wood flour acts only as a filler without reinforcing potential. Comparing pulp fibre types, TMP provided the highest tensile and impact strength properties even though the fines content was the lowest. One explanation for this behaviour is that TMP fibres are stiffer than chemically bleached fibres. It is also suggested that the hydrophobic lignin component in TMP fibres might act as a compatibiliser between the PLA polymer and the fibres, improving the fibre-matrix adhesion. [74]

Comparing chemical pulp fibres, softwood kraft pulp provided the highest composite strength properties, probably due to their better fibre dispersion in the polymer matrix, even though the retained aspect ratio was lower and fines content higher than with hardwood kraft pulps. The differences in fibre dispersion and possibly distorted fibre dimension measurements lead to a fact that no straight conclusions between aspect ratio and mechanical performance of the composites can be made.

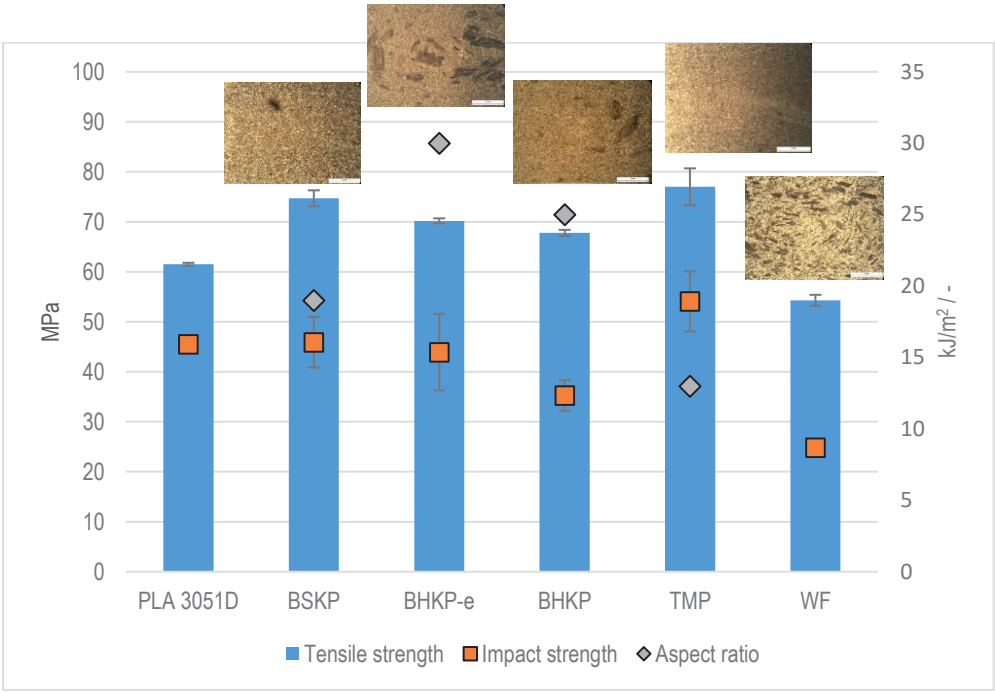


Figure 19. Comparison of mechanical properties, aspect ratio and fibre dispersions of PLA biocomposites reinforced with 30 wt-% of wood based fibres from different sources. Picture adapted from the results obtained in Publication II.

Also recycled fibres show potential as PLA reinforcement, improving both tensile strength and stiffness of the composites, while keeping impact performance on the same level with neat PLA (Publication IV). When fibre types are compared, LPB fibres showed the overall best performance (Figure 20.). LPB fibres include mechanical pulp in addition to chemical fibres, which could partly explain the improved properties. LPB fibres have also higher hydrophobic characteristics due to hydrophobic resins added in the board making process. In addition, fines content of LPB was lower, improving reinforcing and dispersing capability of the fibres in composite structure. Regarding fibre sludge, it shows similar effects than wood flour when combined with ONP fibres, and therefore can be regarded as low-cost filler that has the ability to improve composite stiffness.

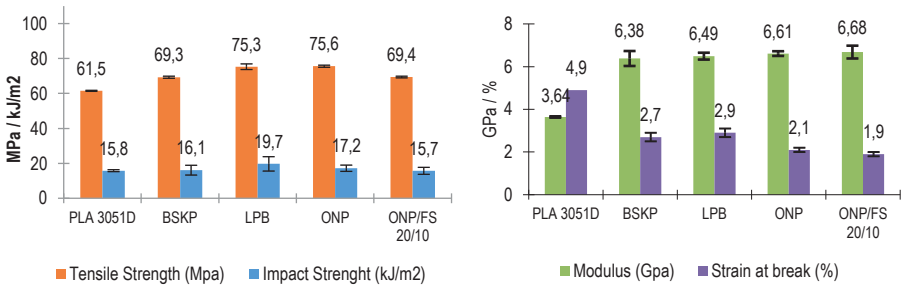


Figure 20. Mechanical properties of PLA composites including 30 wt-% of various recycled fibres

7.4 Extrusion foaming of pulp fibre biocomposites

The effect of pulp fibres on foamability of PLA biocomposites was studied in Publication V. The addition of 10 and 20 wt-% of bleached kraft pulp fibres using either carbon dioxide or isobutane as blowing agents allowed the production of low density foams (densities less than 0,2 g/cm^3). Addition of fibres suppressed expandability especially with higher fibre content, as seen from narrower strand profiles (Figure 21.), reflecting also to density values shown in Table 15. With 10 wt-% of fibre loading, the effect of fibres on expansion ratio and density was relatively low. The reduced foamability was expected, as fibres restrict the foamability of the matrix polymer mechanically, and more importantly, the relative amount of PLA is lower as it has been partially replaced by fibres that are not able to be foamed in themselves. In addition, wood-based fibres have higher inherent density compared to PLA (1.4 vs 1.24), which partly plays role in lower density reduction.

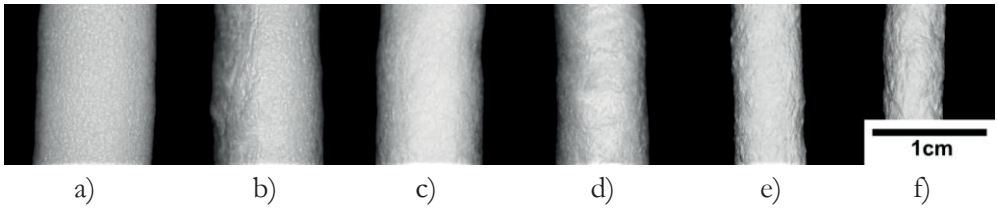


Figure 21. Side profiles of extrusion foamed pulp fibre reinforced PLA biocomposites with chain extension. a) PLA+isobutane; b) PLA+CO_2; c) PLA+10 wt% BHKP+isobutane; d) PLA+10 wt% BHKP+CO_2; e) PLA+20 wt% BHKP+isobutane; f) PLA+20 wt% BHKP+CO_2

Table 15. Densities of extrusion foamed pulp fibre reinforced PLA biocomposites

Material	Isobutane	Carbon dioxide
PLA	0,06 g cm^{-3}	0,05 g cm^{-3}
PLA + 10 wt-% BHKP	0,07 g cm^{-3}	0,07 g cm^{-3}
PLA + 20 wt-% BHKP	0,13 g cm^{-3}	0,14 g cm^{-3}

By examining the cellular structures of produced biocomposite foams by SEM imaging, it can be seen that the presence of fibres reduces the average cell size and increase the cell density (Figure 22.). The same phenomena has also been reported in previous studies. [88],[89],[93] The presence of fibres also seem to hinder cell growth, also shown by Koyama et al. [131] Due to small cell size, the cells are less susceptible to cell rupture and coalescence, allowing also lower cell size distribution. As shown before [89],[92],[93], fibres also act as nucleating sites, promoting cell nucleation and causing therefore formation of smaller cells. The addition of higher fibre content seems to deteriorate cell structure, especially with carbon dioxide as blowing agent. When the two blowing agents are compared, isobutane provided somewhat lower cell sizes and improved cell structure in biocomposites containing 20 wt-% of pulp fibres.

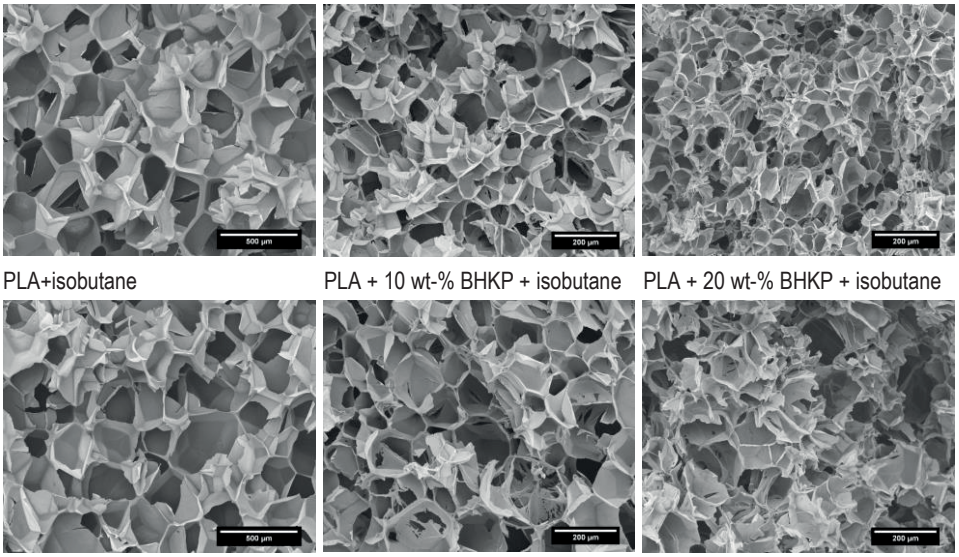


Figure 22. SEM pictures of extrusion foamed pulp fibre reinforced PLA biocomposites

8 CONCLUSIONS AND FUTURE OUTLOOK

Wood-based fibres have gained increasing interest as biocomposite reinforcement with existing commercial applications. However, to date, matrix materials have mostly consisted of fossil-derived or non-biodegradable plastics. To complement the existing materials, industrially compostable PLA-based biocomposites can provide an alternative end-of-life possibility in addition to lower environmental footprint compared to fossil-derived materials. In this study, the main target was to provide more information of utilisation of wood fibres as PLA reinforcement in injection moulded and extrusion foamed applications. The study concentrated on effect of melt processing on fibre morphologies, as well as the effect of various fibre treatments and wood fibre source on PLA biocomposite performance. In addition, the study covered the effect of wood fibre reinforcement on foamability of PLA.

Melt processing of PLA-based biocomposites had inevitable effect on fibre morphologies of wood-based fibres (*Research question 1*). All compared fibre types were shortened length-wise during melt processing steps due to occurring high temperatures and shear forces. Fibre attrition was higher with longer fibres, which led to fibre length reduction to the same level regardless of fibre type. On the other hand, fibre widths remained unchanged, and therefore it can be concluded that the aspect ratio, as one of the key reinforcing factors of wood fibres, was affected by the remaining fibre length and initial fibre width of the fibres. Industrial bleaching of hardwood kraft pulp fibres led to higher fibre attrition during processing possibly due to higher refinability of the bleached fibres compared to unbleached ones. Attrition can be reduced by utilisation of epoxidated linseed oil, which lubricates the fibres and therefore decreases the fibre friction during processing. While fibre dispersion was adequate with all fibre types, the best dispersion was obtained by utilisation of loose fibre pellets and longer screw length in twin-screw extrusion process.

Reinforcing effect of wood fibres was found to depend on the retained fibre length after processing, fibre dispersion and fibre-matrix adhesion, consistent with short-fibre composite theories (*Research question 2).* Industrial fibre bleaching resulted

in higher fibre attribution and therefore, to lower reinforcing capability compared to unbleached fibres from the same batch. On the other hand, the residual surface lignin of unbleached fibres indicated improvement of the fibre-matrix adhesion. The effect of lignin as adhesion promoter was also supported by improved composite performance of TMP fibres, even though fines content and fibre length was significantly lower than in kraft pulp fibres. The differences in dispersion reflected mechanical properties somewhat, when various wood fibre types were compared. Due to differences in fibre dispersion, no straight conclusions could be made between fibre aspect ratio and composite physical performance. Recycled fibres also showed potential as fibre reinforcement for PLA: especially fibres from liquid packaging board showed improved performance, having hydrophobic surface characteristics due to hydrophobic resins.

Fibre surface treatments do have an affect the mechanical performance of wood fibre reinforced PLA biocomposites (*Research question 3*). Utilisation of unbleached kraft pulp fibres showed great potential as PLA reinforcement, improving the mechanical properties significantly due to the reasons described in research questions 1 and 2. Surface compatibilisation with epoxidated linseed oil provided lower fibre attrition and compatibilising effect especially for bleached hardwood kraft pulp fibres. Regarding physical fibre treatments, dry-refining of BSKP fibres resulted in reduction of all measured properties due to high fines content and poor fibre dispersion. In fractionation studies of TMP fibres, removing the fines from TMP resulted in more uniform fibres with improved dispersing capability were achieved, providing improved composite mechanical properties. Fibrillation of fibre surfaces decreased composite performance, attributed to increased bonding capability and fines content, and higher fibre attrition during processing.

Wood fibre-based PLA composites are also applicable for extrusion foaming (*Research question 4*). Even though the expandability of thermoplastic material is expected to decrease when non-foaming material is added to the system, low-density foams were produced both with 10 and 20 wt-% of fibre content with selected physical blowing agents (CO_2 and isobutane). The 10 wt-% fibre addition had relatively low effect on PLA expansion ratio and density. The addition of fibres reduced the average cell size and increased cell density of PLA, indicating that fibres act as nucleating sites promoting cell nucleation. Isobutane as a blowing agent provided less deteriorated cell structure with lower cell sizes especially with biocomposites containing 20 wt-% fibre content.

As an overall conclusion, wood fibres have great potential as PLA reinforcement influenced by the fibre morphologies. The material is suitable both for injection moulded as well as extrusion foamed applications with improved properties. The study verifies the importance of fibre dispersion and fibre-matrix adhesion in wood-fibre reinforced PLA composites. Strong bonding capability of wood-based fibres with each other need to be diminished by minimising the fibre fines content in the composite material by correct fibre selection or fibre fractionation, and utilising dispersing agents on the fibre surface. Wood fibres show relatively good natural adhesion to PLA, but further improvements can be reached by utilisation of surface lignin or bio-based compatibilisers. In addition to polymer and processing parameter selection, fibre attrition during melt processing can be controlled by fibre type, fibre fractionation and use of compatibilising agents. The presence of fines seem to have a negative affect both on adequate fibre dispersion as well as reinforcement capability due to higher intermolecular forces between the fibres, but the outcome depends on other factors, as well.

This study provides novel understanding on wood fibre reinforcement of PLA-based materials. It acts as a basis for further developments towards commercial, high-volume products to be used in several applications. Further research should be targeted to optimisation of process parameters for industrial-scale processes to ensure high throughput with adequate material properties for targeted product. By fractionation of wood-based fibres to controlled fibre distributions without the presence of fines, reinforcing capability of the fibres could be further increased or optimised. On the other hand, the conducted studies did not take porosity into consideration as an additional factor affecting the biocomposite performance. Utilisation of unbleached fibres can enable significantly increased composite performance without the need of bleaching process, but requires more research on different unbleached fibre types and their effect on mechanical properties, as well as operational aspects in pulp factories to ensure viable feedstock. The use of high heat PLA types can provide added-value properties for wood-based biocomposites by introducing higher thermal stability especially in injection moulded or extrusion foamed products used e.g. outdoors or as insulation.

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PUBLICATIONS

PUBLICATION I

Influence of pulp bleaching and compatibiliser selection on performance of pulp fibre reinforced PLA biocomposites

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Journal of Applied Polymer Science 136 (37) (2019) 47955
https://doi.org/10.1002/app.47955

Journal of Applied Polymer Science

Influence of pulp bleaching and compatibilizer selection on performance of pulp fiber reinforced PLA biocomposites

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ABSTRACT: This article focuses on the effect of pulp bleaching and emerging commercial compatibilizers on physical performance of pulp fiber reinforced poly(lactic acid) (PLA) biocomposites. Industrially bleached and unbleached hardwood kraft pulp fibers are treated with several additive types, and compounded with PLA to fiber content of 30 wt %. After injection molding, the produced biocomposites are evaluated by their mechanical performance and fiber–matrix adhesion. For selected materials, fiber surface and fiber properties are reflected to composite performance by analyzing the compositions, dimensions, and lignin coverage of original fibers, as well as fiber dispersion and dimensions after melt processing. As a conclusion, unbleached kraft pulp fibers provide significant improvement in physical properties of PLA/pulp fiber composites. Of the screened compatibilizers, epoxidated linseed oil has a clear positive effect on performance when bleached kraft pulp fibers are used. The improvements correspond to enhanced fiber–matrix adhesion and differences in remaining fiber length distributions. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 47955.

KEYWORDS: adhesion; biocomposite; poly(lactic acid); pulp fibers; wood-based fibers

Received 4 February 2019; accepted 30 April 2019
DOI: 10.1002/app.47955

INTRODUCTION

In recent years, bio-based material solutions, including biocomposites, have gained significant interest due to increasing environmental awareness, material recycling incentives, increasing government legislations, and tightening CO_2 regulations. In conventional wood plastic composites, wood flour is typically used as a cheap filler, providing increased stiffness without significant improvements in other physical or mechanical properties. To achieve additional reinforcement, such as strength and impact resistance, a fiber with a higher aspect ratio is required, such as wood pulp or cellulose fibers.[1,2] In addition, wood pulp fibers share the same positive environmental performance as wood flour, being sustainable, affordable, easily available, and nonabrasive in thermoplastic melt processing methods.

Now, various wood fiber reinforced biocomposite materials based on oil-based polyolefins such as polypropylene (PP) and polyethylene (PE) have entered the markets.[3–5] While these composites have some environmental benefits and some of them are based on recycled polymers, they still relay on fossil-derived, noncompostable polymer materials and show significant challenges in recycling. As an alternative, poly(lactic acid) (PLA) provides a bio-based and industrially compostable polymer matrix option for biocomposite production. Among the available bio-based polymers, PLA is one of the few bio-based polymers produced at commercial scale. PLA can be processed with conventional thermoplastic processing methods, allowing simplified commercial uptake.[6] In general, PLA has good strength with relatively low oxygen barrier properties and good film transparency, enabling, for example, the production of breathable films. However, the drawbacks of PLA are its low heat deflection temperature and brittleness.[7] These drawbacks can be reduced, for example, by controlling the crystallization behavior via nucleation[8] or stereochemical structure of PLA,[9] enabling also commercially available high-temperature resistant PLA grades.

Wood-based fibers have varying characteristics depending on their source.[10] In the case of pulp fibers, the fiber properties differ also depending on the separation method, known as pulping. In chemical pulping, chemicals are used for lignin degradation and dissolving. Together with high temperature and pressure, chemical pulping separates the fibers without the need for mechanical treatment, resulting to removal of about 50% of wood material.[11] Within chemical pulping,

kraft (sulfate) pulping is by far the most common pulping process currently in operation.[12] After the kraft pulping, unbleached kraft fibers contain 2–4.5% residual lignin. The residual lignin is the major contributor to the pulp fiber color,[13] thus bleaching is utilized to remove the remaining residual lignin to obtain a white cellulose pulp. In addition to brightness, bleaching helps to clean the pulp and help to reduce shives and bark debris.[13] The bleaching chemicals also dissolve the pulp extractives. With the removal of residual lignin in the bleaching process, fibers can swell more freely, increasing both flexibility and pliability of the fibers.[14] Due to the advantages of industrial bleaching process, 70% of the 137 million tons of chemical pulp produced annually is bleached.[15] However, the use of strong chemicals in bleaching result in weaker fibers due to decrease of cellulose molecule length.[16]

One key parameter for a fiber to be able to reinforce a composite material is critical fiber length.[17] Critical fiber length is defined by fiber diameter, fiber tensile strength, and strength of the fiber–matrix bond. The critical fiber length is proportional to the fiber diameter; thus, fiber reinforcement capability can be evaluated by fiber aspect ratio (length of the fiber divided by the fiber diameter/width). As an example, calculated critical fiber length for radiata pine pulp fibers is around 0.8 mm (aspect ratio ~35),[18] but the critical fiber length is found to vary depending on fiber type, modification, type of matrix polymer and fiber content.[19]

For optimal fiber–matrix bond, fibers need to be well dispersed in the polymer matrix to achieve connection between individual fibers and matrix polymer.[20] Shear forces during melt processing enable the needed fiber dispersion by breaking up fiber agglomerates and distributing the fibers within the molten polymer. However, natural fibers are sensitive to these shear forces and the elevated temperatures present in melt processing. Thus, fiber length is reduced during compounding and injection molding.[21] In the case of PP/wood fiber composites, the composite physical performance has been shown to have a low correlation with fiber lengths,[18] fiber types,[2] and pulping conditions.[22] However, due to the interdependence of several parameters affecting the composite performance, no comprehensive conclusions have been possible so far.

In general, the interfacial bond or adhesion between lignocellulosic fibers and PLA is naturally strong with considerable specific interactions between the components.[23] However, further improvements have been achieved by several strategies, such as addition of external additives,[24] acetylation,[25] maleic anhydride treatments,[26] silane,[27] and alkali[28] treatments. Ideally, from an industry point of view, the composite materials and processing methods should be as simple, affordable, and effective as possible. External additives have a clear advantage in this regard, compared with chemical modification of fibers (often requiring a separate or additional processing step). Within external additives, especially modified vegetable oils have been suggested as potential compatibilizers in biocomposite applications due to their sustainability, availability, and relatively low cost.[29] Specifically, epoxidated linseed oil (ELO) has been highlighted as a potential candidate, acting as both a reactive plasticizer and a combined plasticizer-coupling agent in PLA—bleached softwood kraft pulp composites.[30]

Previously, the effect of residual lignin and bleaching on pulp fiber biocomposite performance has not received much attention. Rayung *et al.*[31] studied hydrogen peroxide bleaching of oil palm empty fruit bunch fibers in PLA composites. In the study, bleaching improved mechanical properties of PLA by enhancing the fiber/matrix interfacial adhesion and increasing the crystallinity of the fiber with the removal of lignin and hemicelluloses. However, the chemical compositions of the fibers were not addressed by Rayung *et al.*, and the fibers were not treated by pulping process. In a study by Burgstaller *et al.*,[32] unbleached kraft pulp fibers provided reasonable material properties in injection molded PP composites, but the study did not address the effect of residual lignin. Beg and Pickering[33] studied the effect of fiber bleaching on kraft pulp fiber reinforced PP composites. They concluded that the removal of lignin and hemicelluloses improved the interfacial bonding between the fiber and the matrix and increased crystallinity of the fibers, which led to slight improvement of mechanical performance of the composites. In low-density PE composites, commercial batch cooked pulps before bleaching provided better tensile and strain properties compared to bleached fibers.[34] Also the initial fiber properties such as stiffness and tensile strength were higher before bleaching. However, the authors are not aware of any publications in which the effect of kraft pulp fiber bleaching on PLA-based biocomposites has been studied.

The aim of this study is to screen some of the emerging compatibilizer candidates for pulp fiber reinforced PLA composites with regard to the physical performance of the produced biocomposites. In particular, the selected additives are compared to ELO. The study confirms the previous findings that ELO is able to act as an efficient compatibilizer for PLA/pulp fiber biocomposites. Above all, this study compares the effect of unbleached and industrial chlorine dioxide (ClO_2) bleached kraft pulps derived from the same industrial line on the properties of the hardwood kraft pulp fiber reinforced PLA biocomposites. Especially, chemical and physical properties of the fibers are reflected to composite performance by analyzing the fiber compositions, lignin coverage, and fiber dimensions of the bleached and unbleached fibers. The study also addresses how the fiber bleaching, presence of ELO additive, and interaction of bleached and unbleached kraft pulp fibers with the polymer matrix effects fiber attrition and dispersion in melt processing, and therefore also mechanical performance of the biocomposite. As a conclusion, unbleached hardwood kraft pulp (UHKP) fibers provide highly improved physical performance for pulp fiber reinforced PLA biocomposites, attributed to good fiber–matrix adhesion, low fines content and high remaining aspect ratio of the reinforcing fibers. Overall, the study provides novel insight on the effect of bleaching and improves the knowledge of the parameters affecting the performance of PLA–pulp fiber composites, with a view of increased commercial uptake of these totally bio-based and industrially compostable materials.

EXPERIMENTAL

Materials and Processing

Matrix Polymer. NatureWorks Ingeo PLA (NatureWorks LLC, Minnetonka, MN) PLA 3052D was selected as matrix polymer. PLA 3052D is a transparent, bio-based, semicrystalline polymer intended for injection molding applications. The specific gravity, melt flow rate, glass-transition temperature, and crystalline melt temperature of PLA 3052D are 1.24, 14 g/10 min (210 °C, 2.16 kg), 55–60 °C, and 145–160 °C, respectively.[35]

Fibers and Fiber Treatments. UHKP and bleached (BHKP) hardwood (birch) kraft pulp fibers were kindly provided by UPM

Kymmene Oyj (Helsinki, Finland) in never-dried form. Unbleached fibers were collected from the pulp line after acidification in pH of 9–10 from the same batch as bleached fibers. Fibers were delivered to VTT in a dry solid content (d.s.c.) of 10%. Due to alkality of the unbleached fibers, the fibers were washed at VTT in two batches by diluting the pulp to d.s.c. of 4% and then thickening it to 10%. The washing sequence was repeated five times, with diffuse time of 10 min between the sequences. After washing, the pulp batches were mixed together, centrifuged to 35% d.s.c., homogenized, and fractioned by removing large fiber chips to enable fiber feeding in compounding step. In the case of ClO_2 bleached fibers, the excess water was removed from the never-dried fibers by centrifugation to d.s.c. of 35%. Afterward, the big fiber cakes were broken up in a Forberg batch mixer (Forberg International AS, Oslo, Norway) and the surface additives (shown in Table I) were introduced by spraying them onto selected fiber surface in mixing stage to concentration of 5 wt % with respect to fibers, except for granulate form Vinnex, which was added in the compounding stage. The additive selections were made based on results shown by Immonen *et al.*[36,37] The final selection of compatibilizers was made to cover a suitable range of reactive chemistry and functionalities.

After additive treatments, fibers were compacted to fiber pellets using a VTT E-Compactor[38] to enable adequate feeding in compounding. After compacting, the pellets were gently broken down to slightly fluffier form by running the pellets through twin-screw feeder to assure good fiber dispersion during compounding.

Composite Processing. Compacted UHKP and BHKP fibers, with and without additives, were compounded with PLA to a fiber content of 30 wt % using a corotating twin-screw extruder (Berstorff ZE 25x48D; Berstorff GmbH, Hannover, Germany). To feed the materials, gravimetric feeders and a temperature gradient from 40 °C in the feeding section to 190 °C in the melting zones and the die, and a screw speed of 200 rpm were used. The fibers were fed from the first heating zone in d.s.c. of about 90%. Small amount of moisture in pulp fibers has been shown to preserve the fiber length during melt processing without significantly affecting the mechanical properties of the PLA composites through PLA degradation, when excess water is removed by effective vacuuming.[39] The processing setup is schematically illustrated in Figure 1, and the different material combinations are shown in detail in Table II. After compounding, the compounds were injection molded using a cold mold with an injection-molding (Engel ES 200/50 HL, Engel Austria GmbH, Schwertberg, Austria) into ISO 3167 tensile test specimens with a length of 150 mm and a 10 mm wide by 4 mm thick by 80 mm long midsection. In addition to the composite samples, specimens from neat matrix polymers were produced as reference materials. After injection molding, the tensile test specimens were stored in a room with standard conditions (23 °C, 50% relative humidity) for at least 5 days before testing.

Fiber Characterization

Chemical Composition of the Fibers. For the chemical analyses of the fibers, the samples of UHKP and BHKP were air-dried and ground using Wiley mill (Thomas Scientific Inc., Swedesboro, NJ). Chemical composition was determined according to the modified NREL method.[40] The extractives content of air-dried samples were determined gravimetrically after Soxhlet extraction with heptane. For carbohydrate analysis and lignin content determination, the sample after heptane extraction was hydrolyzed with sulfuric acid. Acid hydrolysis was performed using 70% H_2SO_4 for 1 h at 30 °C followed by dilution to 2.5% acid concentration and autoclave treatment of 50 min at 120 °C. The resulting monosaccharide compositions were determined by high-performance anion-exchange chromatography with pulse amperometric detection (Dionex ICS-5000; Thermo Fisher Scientific, Waltham, MA, equipped with CarboPac PA20 column), according to Hausalo[41] and Willför *et al.*[42] The polysaccharide content in the samples was calculated from the corresponding monosaccharides using an anhydro correction of 0.88 for pentoses and 0.9 for hexoses. Klason lignin content, that is, the insoluble residue from the hydrolysis was determined gravimetrically. Acid soluble lignin was determined from the hydrolysate based on ultraviolet at 215 and 280 nm using equation described by Goldschmid.[43] Ash content of the whole material was measured gravimetrically after burning the samples at 550 °C for 23 h.

Table I. Selected Compatibilizers for Screen Series of the PLA/Kraft Pulp Fiber Composites

Trade name and producer	Acronym	Functionality/description	Main application defined by producer
Vikoflex 7190 (Arkema Inc. Colombes, France)	ELO	ELO; primary, polymeric type, plasticizer–stabilizer	Food contact applications, PVC homopolymer and copolymer plasticization and stabilization[44]
Vinnex 2525 (Wacker Chemie AG, München, Germany)	PVA	Poly(vinyl acetate)-based binder	Compostable binder for biopolymer systems, PLA processing improvement modifier[45]
Dynasylan GLYEO (Evonik Resource Efficiency GmbH, Hanau, Germany)	EPX	Bifunctional organosilane with epoxide and triethoxysilyl group	Coupling agent, cobinder/copolymer, crosslinking agent[46]
GENIOSIL XB 502 (Wacker Chemie AG)	SIL	Silicon reinforced polyether-based silane-terminated polymer (alpha-silane technology)	Reactive binder for adhesives, potting compounds and coatings, used especially for bonding wood[47]

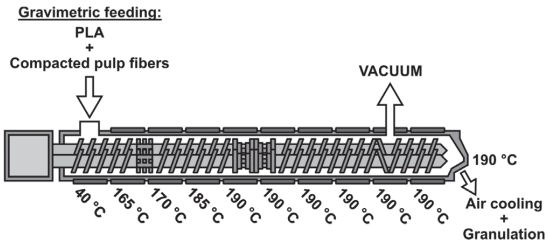

Figure 1. Process setup used in compounding of PLA-fiber composites.

Table II. Compositions of the Produced Samples

Sample code	Polymer (wt %)	Fiber type (wt %)	Surface additive (wt % from fibers)
PLA-neat	PLA (100)	—	— (0)
PLA-UHKP-ref	PLA (70)	UHKP (30)	— (0)
PLA-UHKP-ELO	PLA (68.5)	UHKP (30)	ELO (1.5)
PLA-UHKP-PVA	PLA (68.5)	UHKP (30)	PVA (1.5)
PLA-UHKP-EPX	PLA (68.5)	UHKP (30)	EPX (1.5)
PLA-UHKP-SIL	PLA (68.5)	UHKP (30)	SIL (1.5)
PLA-BHKP-ref	PLA (70)	BHKP (30)	— (0)
PLA-BHKP-ELO	PLA (68.5)	BHKP (30)	ELO (1.5)
PLA-BHKP-PVA	PLA (68.5)	BHKP (30)	PVA (1.5)
PLA-BHKP-EPX	PLA (68.5)	BHKP (30)	EPX (1.5)
PLA-BHKP-SIL	PLA (68.5)	BHKP (30)	SIL (1.5)

Surface Chemical Composition of the Fibers. The surface chemical composition of UHKP and BHKP were analyzed with X-ray photoelectron spectroscopy (XPS), using an AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK) with monochromatic Al Kα irradiation at 100 W, under neutralization. Pure cellulose filter paper (Whatman) was used as an *in situ* reference, as well as for reference for pure cellulose. All samples were pre-evacuated overnight before the measurements. The loose fibers were pressed onto double-sided vacuum tape and inserted into the Axis Ultra. Survey scans as well as C 1s and O 1s high-resolution regions were acquired from two to three locations; the area of analysis area was less than 1 mm^2 while the analysis depth is necessarily typically less than 10 nm. The CasaXPS software was utilized in data analysis, in which the carbon and oxygen contents were each determined from survey scans, while carbon high-resolution data were utilized in further chemical analysis.[48]

Fiber Dimension Analyses. The dimensions of both unprocessed, compacted, and processed fibers were analyzed using automated fiber analyzer L&W STFI FiberMaster (Lorentzen & Wettre, Stockholm, Sweden). To prepare samples for the measurements, 1 g of dry fibers are dispersed in water and soaked in water for at least 4 h to achieve the correct fiber dimensions and obtain individual fibers. The actual measurements are performed based on image analysis by analyzing the length, width, aspect ratio, and fines proportion (fiber length less than 0.2 mm) of the fibers. Each sample included two to three reference measurements. To be able to measure fiber dimensions from biocomposite samples, PLA matrix was dissolved with chloroform to obtain loose fiber samples.

Biocomposite Characterization

Tensile Tests. For analyzing tensile properties of the produced samples, the ISO 527 standard was applied. The measurements were performed using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp.) with 10 kN load cell and a 5 mm min^{-1} crosshead speed at standard conditions (23 °C, 50% relative humidity). The analyzed properties were Young's modulus (GPa, linear regression between the strain of 0.0005 and 0.0025 mm mm^{-1}), and tensile strength (MPa) and strain at break (%). The results were averages of five reference samples.

Impact Strength. The impact strength measurements were performed according to ISO 179 standard using a Charpy CEAST Resil 5.5 Impact Strength Machine (CEAST S.p.A., Torino, Italy). The tests were performed on unnotched specimens using 2 J pendulum. Based on the impact energy (J) measured by the impact strength equipment, the impact strength was then calculated according to formula 1:

$$\text{Impact strength}\left(\frac{\text{kJ}}{\text{m2}}\right) = \frac{\text{Impact energy (J)}}{\text{Width (mm)} \times \text{thickness (mm)}} \times 1000 \quad (1)$$

Fiber–Matrix Adhesion by SEM Imaging. To determine the adhesion between fibers and PLA matrix, a JEOL JSM-6360LV scanning electron microscope (SEM) (JEOL Ltd., Tokyo, Japan) was utilized for SEM analysis of the composites. Cryofractured surfaces of dogbone specimens were qualitatively investigated to evaluate the compatibility between PLA matrix and the fibers.

Fiber Dispersion in Microscopic Means. For the microscale evaluation of fiber dispersion in PLA matrix, thin microtome samples of the composite length-wise cross sections were taken and analyzed using a Wild Heerbrugg M5A stereo microscope (Wild Heerbrugg Ltd., Heerbrugg, Switzerland) applying a magnification of 25×.

X-ray Tomography Imaging. To measure the fiber orientation and diameter distributions in the additive-free BHKP and UHKP biocomposites, samples of PLA-UHKP-ref and PLA-BHKP-ref were imaged using SkyScan 1172 X-ray microtomography device (SkyScan N.V., Aartselaar, Belgium). Identical imaging settings were utilized for both samples. X-ray tube voltage was 40 kV and current 100 μA. No camera pixel binning or X-ray filter was applied. Rotation step of 0.1° was used in 180° scan. One frame exposure time was 2945 ms and average over eight frames were used for each projection image. Tomography image pixel size was 2.66 μm for BHKP and 2.63 μm for UHKP. Reconstruction was performed with the NRecon software utilizing cone-beam algorithm.[49] The postalignment, ring artifact, and beam hardening correction values were 0, 18, and 54% for BHKP and −2, 19, and 45% for UHKP, respectively.

Crystallinity. Differential scanning calorimetry (DSC) measurements were performed to evaluate glass transition, melt temperature, and crystallinity of the samples. The analyses were done using MDSC2920 DSC Thermal Analysis (TA Instruments, New Castle, DE) under nitrogen atmosphere. A total of 7–9 mg of relevant sample was weighted and encapsulated in aluminum crucible. The samples were heated up from 0 to 200 °C and then cooled to 0 °C with a constant heating/cooling rate of 10 °C min^{-1}. From the obtained thermographs, melting temperatures, cold crystallization temperatures, enthalpies of cold crystallization (ΔH_c), and enthalpies of melting (ΔH_m) were analyzed. Based on the enthalpy values, crystallinity of the material can be calculated according to formula 2:

$$\text{Crystallinity}\,(\%) = \frac{\Delta Hm - \Delta Hc}{\Delta Hf} \times 100 \qquad (2)$$

where ΔH_f refers to theoretical heat of fusion of 100% crystalline polymer. In the case of PLA, commonly used value for ΔH_f is 93.1 J g^{-1}.[50] In the case of fiber reinforced materials, PLA weight fraction of the samples was taken into account in the automatic calculations by the DSC program.

RESULTS AND DISCUSSION

Fiber Properties

Before melt processing with PLA, untreated unbleached and bleached fibers were characterized with respect to fiber dimensions, chemical composition, surface lignin (summarized in Table III) and appearance (Figure 2). Fiber dimensions of the utilized hardwood kraft pulp fibers correlate well with literature reference values, having an average length of a little less than 1.0 mm, and width of 20 μm.[10] The results also show that bleaching process does not affect fiber dimensions or fines content of the untreated fibers significantly. As expected, differences can be associated with the change of total lignin contents of the fibers: bleaching removes residual lignin from the fiber as noticed from the data in Table III, resulting in bright white fibers (Figure 2). Based on earlier reports, it is assumed that bleached fibers show increased flexibility and pliability,[14] which empirical evidence confirm, but potentially at the expense of fiber strength due to shortening of the average cellulose molecular weight.[16] Even after bleaching, some residual lignin still remains with the fibers. Regarding fiber surface changes derived from bleaching process, SEM imaging shows clear differences in the fiber surfaces, with more fiber surface fibrillation recorded in the bleached fibers than unbleached fibers (Figure 3).

In an effort to get some preliminary evidence of the role of lignin in these fiber composite architectures, XPS measurements were performed to give an indication of the location of the residual lignin. There are evidence in the literature that lignin might act as a compatibilizer between cellulosic fibers and PLA,[51,52] but for this to be effective, lignin needs to be located on the fiber surface. The XPS results are shown in Figure 4, where the unbleached and bleached samples are depicted together with a pure cellulose reference. In XPS measurements, the analysis depth is less than 5 nm, so the data are obtained from first atomic layers only. In the XPS survey spectra, only carbon and oxygen are seen. In the insert, C 1s high resolution data show the "XPS cellulose signature", that is, peaks for carbon atoms with one and two oxygen neighbors at 286.6 and 288.1 eV in characteristic ratio in all samples.[53] However, the most dominant peak in unbleached sample is at 285 eV, which is indicative of carbon atoms without oxygen neighbors. This peak is characteristic of lignin (where almost 50% of carbon atoms are without oxygen neighbors).[54] This peak is diminished but clearly visible also in the bleached sample, indicating some presence of surface lignin also in BHKP. On the other and, the same CC peak is also shown to be typical for surface contamination and extractives.[54] However, even if the highly intensive lignin peak in UHKP might be partly due to slightly higher extractive content in unbleached fibers (as seen from Table III), unbleached kraft pulp is shown to contain clearly higher surface lignin content compared to bleached fibers,[55] which is consistent to our results and can indicate improved adhesion to PLA matrix.

Table III. Chemical Compositions of UHKP and BHKP Fibers

Analyzed property	Unit	UHKP	BHKP
Total lignin (gravimetric + soluble)	%	3.8	1.5
Extractives	%	0.36	0.21
Cellulose	mg/100 mg (dry)	62.6	64.2
Xylan	mg/100 mg (dry)	21.9	22.6
Glucomannan	mg/100 mg (dry)	0.62	0.58
Ash residue	%	1.02	0.66
Fiber length*	mm	0.91	0.90
Fiber width*	μm	23.2	22.3
Aspect ratio	—	39.5	40.3
Fines content (<0.2 mm)	%	7.0	7.1

Effect of Compatibilizer Selection on Physical Performance of PLA Biocomposites

For cellulose fiber reinforced PP biocomposites, maleic anhydride-grafted PP has become a well-established compatibilizer, which significantly increases the physical performance of the composite.[56] However, PLA-based biocomposites are lacking research of the

Figure 2. UHKP (left) and BHKP (right) fibers compacted for compounding process. [Color figure can be viewed at wileyonlinelibrary.com]

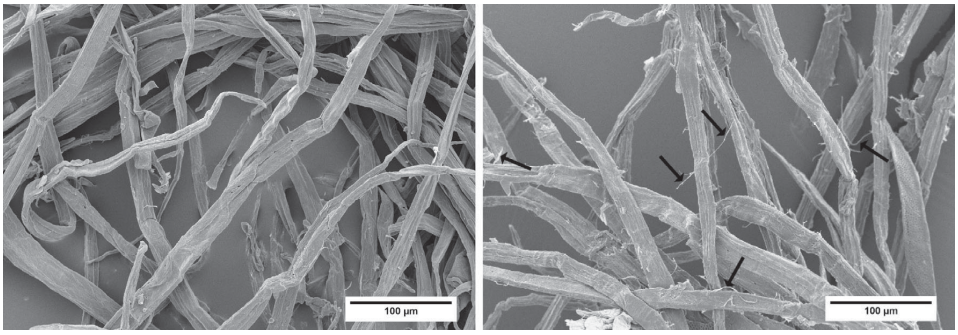

Figure 3. SEM images of UHKP (left) and BHKP (right) fibers. Arrows indicate fibrillation of bleached pulp fibre surfaces.

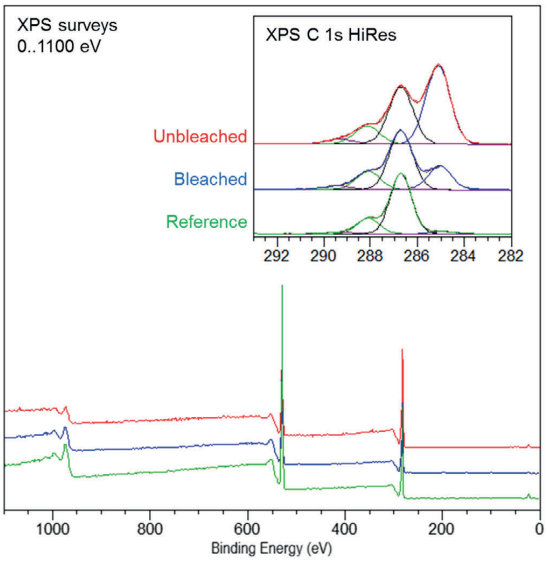

Figure 4. XPS spectra of UHKP and BHKP fibers, together with data from a pure cellulose reference (ash-free Whatman filter paper). High-resolution C 1s regions are depicted in the insert. [Color figure can be viewed at wileyonlinelibrary.com]

possibilities and performance improvements of suitable compatilizing agents, even though PLA has also shown natural adhesion to cellulosic fibers.[23] To increase the understanding of the potentially beneficial compatibilization of PLA-based composites, a broad range of chemistries with an emerging commercial availability were selected to screen their compatibilizing potential. The effect of these additives as adhesion promoters in wood fiber reinforced PLA composites was characterized by means of SEM imaging of fiber–matrix adhesion in combination with mechanical characterization.

The results of the composite mechanical characterization are summarized in Table IV. In the overall interpretation, it can be clearly seen that the addition of 30 wt % pulp fibers to PLA increases all characterized physical properties compared with neat PLA, which is consistent with earlier reports and theory. A notable effect observed was the high overall performance of uncompatibilized UHKP fibers. Uncompatibilized UHKP composites have among the highest, if not the highest, physical performance of all the compositions studied within pulp fiber reinforced PLA composites. This indicates that there is a high degree of wetting and subsequent interfacial adhesion between PLA and UHKP, with supporting data later in this article.

On the other hand, untreated BHKP fibers provide significantly lower mechanical performance to PLA biocomposite. Subsequently, BHKP composites benefit the most from the addition of a compatibilization agent. The significant differences between UHKP and BHKP composites observed can be related to numerous effects, such as fiber attrition during processing, surface wetting, and interfacial bond strength, crystallinity of the polymer and so forth. These differences will be address later in this article.

Of the screened compatibilization agents, GENIOSIL (SIL) shows a clearly reduced fiber–matrix adhesion (see Figures 5 and 6). With both fiber types, SEM images reveal a clear gap in the interface of fiber and matrix polymer, indicating poor fiber–matrix adhesion, with subsequent poor reinforcement of the composites. Of the other screened compatibilization agents, SEM imaging did not reveal any clear differences in the fiber–matrix interfacial bond, indicating reasonable wetting of the fibers. For both fiber types, GLYEO (EPX) showed the highest increase in impact strength. For all other properties, ELO showed the highest physical increases consistently for both analyzed fiber types. Not uncommonly, when material becomes stiffer (increased Young's modulus) through short-chained crosslinking, strain at break, and to some extent tensile strength, tends to decrease. It is therefore interesting to see the rise in all the properties for ELO, which is partly due to long aliphatic alkyl chain (18 carbons) providing some elasticity to coupling.

On the basis of these results, additional characterization was carried out to further study the effect of ELO, the remaining surface lignin of the unbleached and bleached fibers, as well as fiber attrition and dispersion, on the biocomposite performance.

Effect of Fiber Bleaching and ELO Treatment on Composite Performance

For more conclusive results, UHKP and BHKP fibers as PLA reinforcement with and without ELO treatment were studied more

Table IV. Mechanical Properties of UHKP and BHKP Fiber Reinforced PLA Composites with Various Additives

Sample code	Tensile strength (MPa)	Young's modulus (MPa)	Impact strength (kJ m^{-2})	Strain at break (%)
PLA-neat	60.8 ± 0.2	3584 ± 164	16.2 ± 7.2	3.5 ± 0.2
PLA-UHKP-ref	82.5 ± 0.8	6262 ± 219	32.5 ± 20.0	4.6 ± 0.2
PLA-UHKP-ELO	73.1 ± 0.8	6425 ± 205	33.3 ± 9.4	2.8 ± 0.2
PLA-UHKP-PVA	69.2 ± 0.1	6374 ± 159	30.1 ± 15.0	2.1 ± 0.0
PLA-UHKP-EPX	64.8 ± 0.7	6227 ± 349	34.3 ± 24.1	2.5 ± 0.7
PLA-UHKP-SIL	59.4 ± 0.6	6159 ± 173	24.7 ± 12.3	2.2 ± 0.1
PLA-BHKP-ref	67.0 ± 1.4	6144 ± 480	19.7 ± 15.7	2.1 ± 0.4
PLA-BHKP-ELO	79.3 ± 0.7	6509 ± 189	24.8 ± 10.3	3.8 ± 0.2
PLA-BHKP-PVA	73.6 ± 0.3	6106 ± 232	22.6 ± 14.2	3.6 ± 0.2
PLA-BHKP-EPX	66.3 ± 0.6	6174 ± 154	26.2 ± 25.0	1.7 ± 0.2
PLA-BHKP-SIL	67.4 ± 0.5	6070 ± 274	20.9 ± 12.8	3.9 ± 0.1

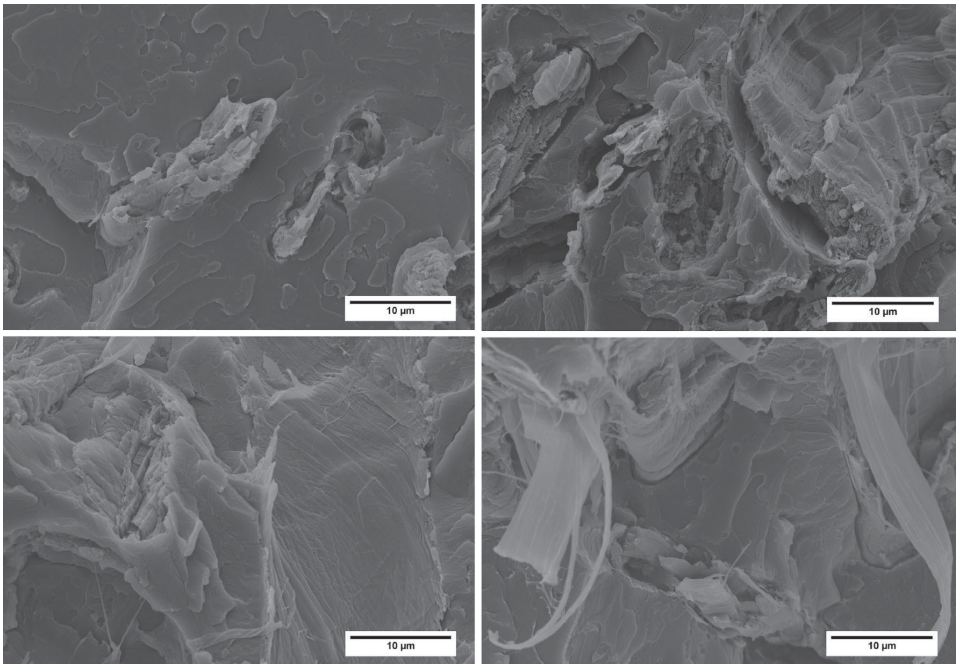

Figure 5. SEM images of PLA + 30 wt % UHKP: top left: PLA-UHKP-ELO; top right: PLA-UHKP-PVA; down left: PLA-UHKP-EPX; down right: PLA-UHKP-SIL.

precisely to understand the underlying phenomena behind (1) kraft pulp fiber bleaching on PLA composite properties, and (2) ELO treatment as adhesion promoter in unbleached or bleached fiber–PLA composites. Thus, in addition to fiber characteristics, average fiber dimensions, fiber dispersion, and composite crystallinity of the produced composites were characterized for the resulting composite materials and reflected to mechanical performance of the materials.

Fiber Dimensions after Melt Processing. The detailed fiber length measurements for all treatments in the study are shown in Table V. Consistent with earlier report,[2] well executed compacting does not decrease average fiber length significantly, but enables adequate fiber feeding to the compounding process. However, fiber length reduces sharply by composite melt processing steps. On the other hand, fiber width tends to remain relatively unchanged during melt processing. It should be noted however, that FiberMaster analysis may make false interpretations of fiber width, as the fibers are no longer round but more flat due to collapse of lumen inside wood fiber walls caused by the fiber processing.[57]

The results reveal that while both fiber types show a reduction in average fiber length during melt processing, bleached fibers show a higher degree of fines generation and fiber length reduction, and as

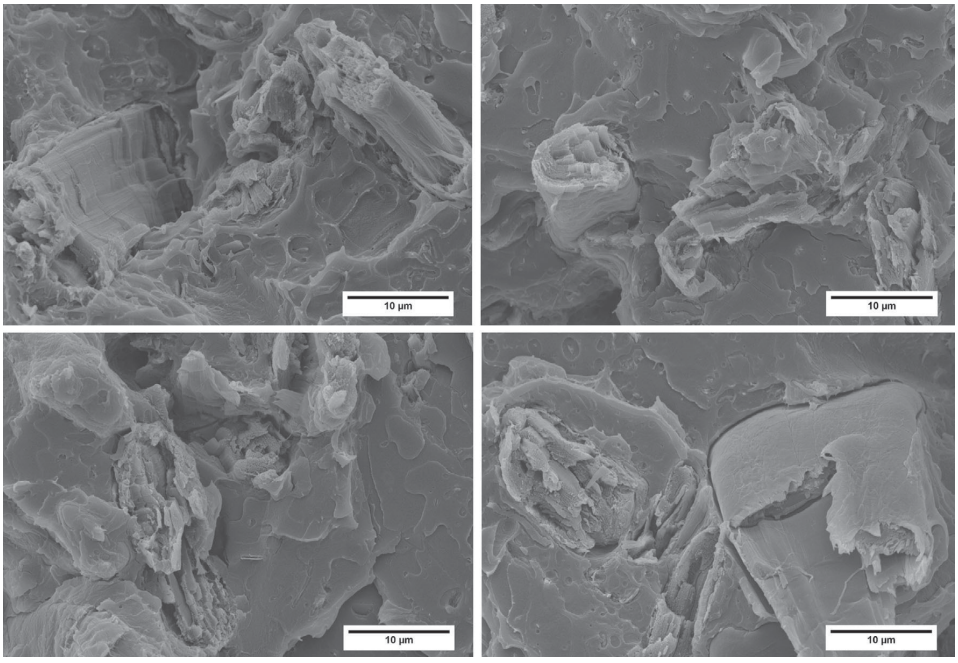

Figure 6. SEM images of PLA + 30 wt % BHKP: top left: PLA-BHKP-ELO; top right: PLA-BHKP-PVA; down left: PLA-BHKP-EPX; down right: PLA-BHKP-SIL.

a consequence, a lower resulting aspect ratio. Bleached fibers are defined as having higher flexibility, with improved refinability, at the expense of fiber strength compared to unbleached fibers.[14,16] Wood fibers mainly fail in melt processing in a polymer matrix via lumen collapse, fiber buckling and subsequent fracturing.[57] The increased refinability of bleached fibers can partially help to explain the fiber attrition process observed in our results. During compacting, however, this process is not observed with only slight effect recorded for fiber length reduction and fines content generation for both bleached and unbleached fibers.

Interestingly, the addition of ELO seams to counter the fiber attrition effect of the bleached fibers, as shown in Table V, and notably, in the significantly lower fines generation. We postulate that ELO, as an oil-based additive, reduces fiber attrition during melt processing by lubricating the fibers and reducing the fiber friction during processing. Retained lignin in the fibers may play a similar role, which can help explain why this effect is less apparent for the unbleached fibers, in combination with less fiber twisting/bending.

Fiber Dispersion. In our previous research, it was noted that kraft pulp fibers disperse well in PLA matrix due to higher shear strength and melt viscosity during melt processing compared to, for example, PP matrix.[2] Similarly, adequate fiber dispersion was recorded in this study, as shown in Figure 7. All the samples show separate fibers without significant fiber flocculation or agglomeration. Uniform

Table V. Fiber Dimensions of the Analyzed Samples

Fiber type	Processing method	Average fiber length (mm)	Average fiber width (µm)	Aspect ratio (–)	Aspect ratio change (%)	Average fines content (%)
UHKP	Original	0.92 ± 0.00	23.2 ± 0.1	39.5	0.0	7.0 ± 0.3
UHKP	Compacted	0.88 ± 0.01	23.6 ± 0.1	37.2	−5.9	5.8 ± 0.6
UHKP	Processed	0.62 ± 0.03	24.3 ± 0.6	25.7	−34.9	11.7 ± 1.1
UHKP-ELO	Compacted	0.91 ± 0.00	24.1 ± 0.0	37.6	−5.0	5.0 ± 0.6
UHKP-ELO	Processed	0.66 ± 0.01	24.8 ± 0.0	26.4	−33.1	10.4 ± 1.3
BHKP	Original	0.90 ± 0.02	22.3 ± 0.1	40.3	0.0	7.1 ± 0.5
BHKP	Compacted	0.81 ± 0.01	22.9 ± 0.1	35.2	−12.7	6.4 ± 0.6
BHKP	Processed	0.44 ± 0.01	25.5 ± 0.1	17.3	−57.0	32.3 ± 2.2
BHKP-ELO	Compacted	0.83 ± 0.01	23.1 ± 0.1	36.1	−10.4	5.6 ± 0.5
BHKP-ELO	Processed	0.52 ± 0.04	26.13 ± 0.9	19.8	−50.9	19.9 ± 1.1

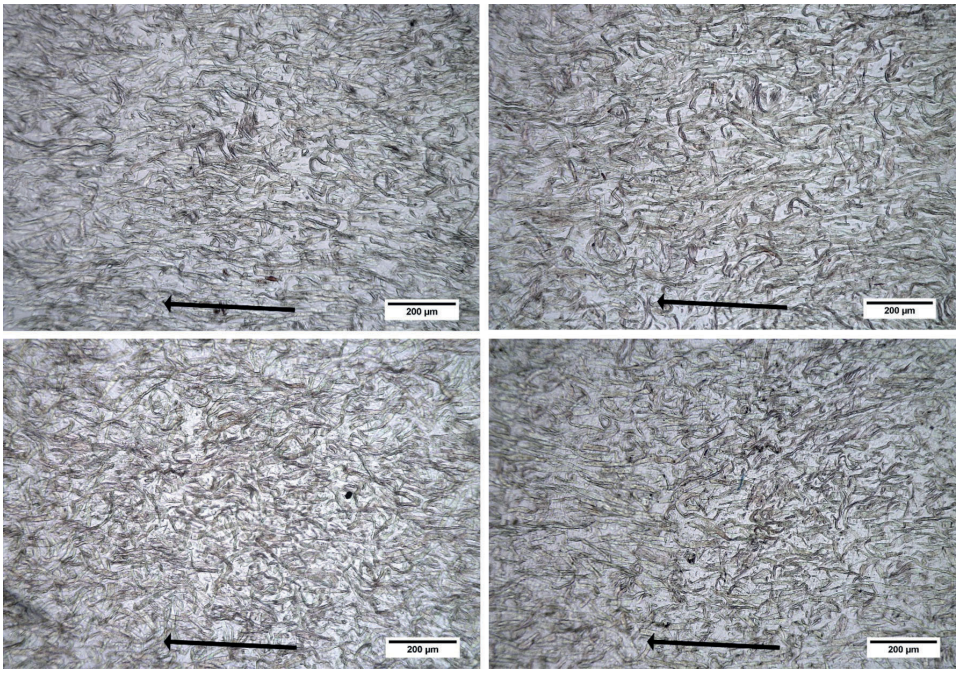

Figure 7. Visualization of fiber dispersion in PLA matrix by microscopic imaging. Up: UHKP, untreated (left), ELO treated (right). Down: BHKP, untreated (left), ELO treated (right). Melt flow direction indicated with black arrow. [Color figure can be viewed at wileyonlinelibrary.com]

fiber dispersions of the samples are also verified by X-ray tomography imaging, showing three-dimensional pictures of undisrupted composite samples of composites containing untreated unbleached and bleached pulp fibers (Figure 8). Both analyses reveal fiber orientation in melt flow direction, as expected by injection molding process, with some degree of fiber curving or twisting.

Crystallinity of the Composites. Crystallinity is one of the main characteristics that define physical properties of a polymeric material. Due to higher intermolecular bonding, crystalline phase provides increased strength properties.[58] In general, conventional injection moldable PLA has slow crystallization rate, thus resulting in a predominantly amorphous polymer material when cold molding and fast cycle time are used.

Table VI shows cold crystallization and melting enthalpies, and the resulting crystallinity, of the material combinations in this study. The data have been retrieved from the first DSC heating to maintain the same thermal history as in the produced and tested composite samples. As expected, neat PLA without fiber reinforcement has not crystallized during processing. When fibers are added, the reinforcement generates increase in crystallization rate. This is due to the nucleating effect of the cellulose fibers during cooling of PLA composites, as previously described by Espinach *et al.*[59] and Masirek *et al.*[60] The use of unbleached fibers resulted in higher crystallinity compared to bleached fibers, with a further increase with the addition of ELO. The higher crystallinity of UHKP fibers compared to BHKP was somewhat unexpected. While cellulose surfaces are well known to act as nucleating sites, we did not expect surface lignin to have such strong effect, even though lignin has been shown to promote PLA nucleation.[61] To make comprehensive conclusions, more experiments would be needed. Regarding improvement by ELO, similarly to poly(ethylene glycol) (PEG) addition to PLA–hemp composites,[60] we propose that ELO, acts as an additional nucleating agent, thus increasing the total recorded crystallinity of the composites. However, ELO decreases the glass-transition temperature of the composites due to plasticization effects, as shown previously by Chieng *et al.*[62]

Normalized Mechanical Properties. To detect the percentual change of mechanical performance compared to PLA and reflect them to other performed analyses, normalized elastic modulus,

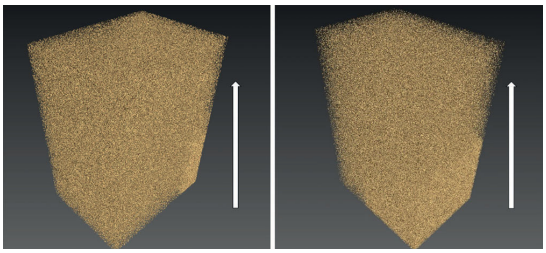

Figure 8. X-ray tomography images of UHKB (left) and BHKP (right) composites. White arrow indicates melt flow direction. [Color figure can be viewed at wileyonlinelibrary.com]

Table VI. DSC Results of the Produced Biocomposites

Sample	Glass-transition temperature (°C)	Melt temperature (°C)	Enthalpy of cold crystallization (ΔH_c) (J g^{-1})	Melting enthalpy (ΔH_m) (J g^{-1})	Crystallinity (%)
PLA-neat	58.8	153.0	23.0	−24.0	1.1
PLA-UBHKP-ref	57.5	155.0	23.0	−33.4	11.2
PLA-UBHKP-ELO	56.1	154.7	21.0	−33.8	13.8
PLA-BHKP-ref	58.1	155.5	24.7	−31.9	7.7
PLA-BHKP-ELO	55.8	154.7	20.6	−29.1	9.1

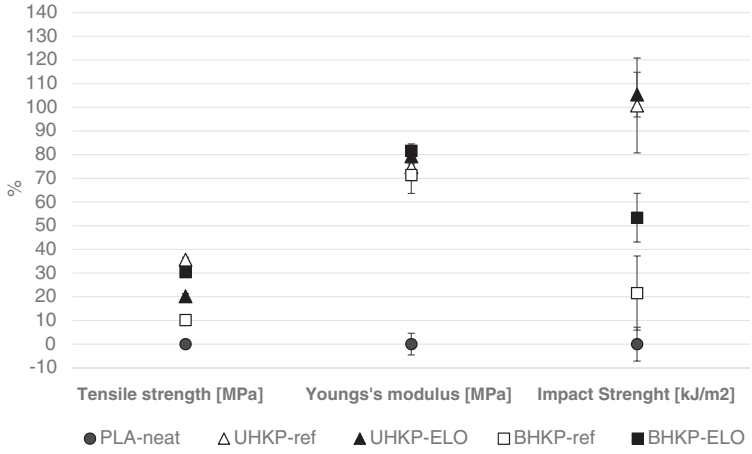

Figure 9. Normalized mechanical properties with respect to neat PLA.

tensile strength, and impact strength values of the unbleached and bleached pulp fiber composites with and without ELO treatment with respect to neat PLA are shown in Figure 9.

Similar to other fibers and fillers,[2,63,64] pulp fibers increase the stiffness of the PLA matrix. ELO increased this even further for all the material combinations in this study. In the case of bleached fibers, ELO addition also significantly improves both tensile strength and impact strength. This is because ELO acts as a reactive compatibilizer between fibers and PLA matrix.[30] In addition, as discussed earlier, ELO treatment minimizes fiber length reduction during melt processing, thus increasing the reinforcement potential of the fibers. On the other hand, the molecular weight of the linseed oil is low enough that it cannot be ruled out that some of the oil penetrates into the fiber and crosslinks internally in the fiber as well, especially in the case of the swollen bleached fibers. This is based on the fact that low-molecular-weight polymers and oils, such as PEG and linseed oil, are known to be able to interact with wood by penetrating into the wood cell walls.[65,66]

However, for unbleached fibers, the ELO treatment has a neutral or slightly negative effect. Introduction of ELO decreases the tensile strength of the composite, whereas impact strength remains largely unaffected. The surface lignin on unbleached fibers might interfere with the compatibilizing effect of ELO, with a less efficient crosslinking between matrix and fiber. Bleached fibers are less crystalline and there are more available hydrogen for ELO to react than in unbleached fibers.[67] Untreated UHKP fibers provide the highest mechanical performance also compared to bleached fibers with or without ELO treatment. This effect is expected, given the higher fiber aspect ratio and lower fines content of unbleached fibers. Also, fiber surface lignin, detected by XPS analysis, probably improves compatibility between unbleached fibers and PLA matrix.

CONCLUSIONS

Concluding the effect of industrial bleaching of kraft pulp fibers, the results show a significant improvement in physical properties when UHKP fibers are used as PLA reinforcement compared to bleached fibers. There can be several factors contributing to this, including compatibilizing capability of the residual lignin on the fiber surface, increased fiber dispersion, fiber alignment, and higher fiber length distribution. The results of this study indicate that bleached pulp fibers are shortened more than unbleached ones during melt processing, which reduce their reinforcement capability. Especially, the fines content is increased significantly compared to unbleached fibers. Fiber dispersion of the composites reinforced with unbleached and bleached fibers is shown to be adequate in both cases. This limits the reasons behind the increased physical performance mainly to the physical performance of the fiber itself or the improved compatibility between the cellulosic fiber and the PLA

matrix. A slight difference in crystallization rate between unbleached and bleached fibers is also expected to affect the mechanical performance in some extent. With the recovery of the physical performance provided by ELO in bleached pulp fiber composites, we conclude that the main contributing factor to the improvement of UHKP versus BHKP fibers is caused by compatibilization capability of surface lignin on fiber surface together with higher fiber aspect ratio and lower fines content in the biocomposite.

Of the screened compatibilizers, ELO showed a remarkable improvement in bleached kraft pulp fiber/PLA composites compared to untreated fibers. Not only does the ELO promote the fiber matrix adhesion, it also helps to reduce fiber attrition during melt processing. The performance of the other compatibilization agents had limited or negative effects on the physical performance in the produced PLA biocomposites. This was particularly apparent in case of the polyether-based silane-terminated polymer (GENIOSIL). Even though, GENIOSIL is targeted for bonding wood with, for example, metals, it did not have adhesion toward PLA with a subsequent lack of chemical bond or compatibility in these systems.

ACKNOWLEDGMENTS

Part of the research has been funded by the CLIC Innovation Ltd New Fiber Products Project (https://clicinnovation.fi/projects/new-fiber-products/). This work was a part of the Academy of Finland's Flagship Programme under project nos. 318890 and 318891 (Competence Center for Materials Bioeconomy, FinnCERES).

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PUBLICATION II

Wood based PLA and PP composites: Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties

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Composites: Part A. 61 (2014) 13-22
https://doi.org/10.1016/j.compositesa.2014.02.002

Composites: Part A 61 (2014) 13–22

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Wood based PLA and PP composites: Effect of fibre type and matrix polymer on fibre morphology, dispersion and composite properties

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ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 29 January 2014
Accepted 1 February 2014
Available online 8 February 2014

Keywords:
A. Wood
A. Fibres
A. Thermoplastic resin
B. Mechanical properties

ABSTRACT

This study presents a comparison of the effect of various wood fibre types in polylactic acid and polypropylene composites produced by melt processing. The study also reveals the reinforcing effect of pelletised wood fibres compared to conventionally used wood flour or refined fibres. Composites containing 30 wt.% of chemical pulps, thermomechanical pulp and wood flour were produced by compounding and injection moulding. Fibre morphologies were analysed before and after melt processing. The dispersion of the fibres and mechanical performance of the composites were also investigated. Fibre length was reduced during melt processing steps, reduction being higher with longer fibres. Wood fibres provided clearly higher plastic reinforcement than wood flour. Comparing the wood fibre types, TMP fibres provided the highest improvement in mechanical properties in polylactic acid composites with uniform fibre dispersion. In polypropylene composites, fibre selection is not as crucial.

1. Introduction

Wood flour is used widely as filler for plastic materials due to its low price, easy availability and bio-based nature. However, there is an increasing interest in using wood fibres instead of wood flours: the fibre shape can provide reinforcement instead of just filling and therefore increase mechanical properties of the composite material [1]; [2]. Typical wood plastic composites (WPC's) are based on polypropylene (PP), polyethylene (PE), or polyvinyl chloride (PVC) matrix filled with wood flour [3]. In addition to using conventional WPC matrix polymers, there are also studies related to, e.g. polystyrene (PS) [4] and polylactic acid (PLA) [5]; [6] matrixes, from which especially PLA as a bio-based and compostable polymer has been of growing interest.

The characteristics of wood fibres depend mostly on their source. The average lengths of softwood and hardwood fibres are 3.3 and 1.0 mm, diameters 33 and 20 μm, stiffness 10–50 and 10–70 GPa, and strength 100–170 and 90–180 MPa, respectively [7]. The fibre pulps produced by paper making industry also differ from their properties depending on how the fibres are separated. Two common pulp types utilized in the paper industry are chemical and mechanical pulp. In chemical pulping, the fibres are separated by dissolving and removing the lignin that bonds fibres together resulting for long and less damaged fibres, whereas in mechanical pulping lignin is softened with heat and repeated mechanical stress. Therefore, mechanical pulps contain a high amount of lignin whereas chemical pulp is almost lignin free. In addition, the fibre length distribution is wider and fines content is higher in mechanical than chemical pulps. In the literature, mechanical pulp fibres are described as more stiff, coarse and straight than chemical pulp fibres [8].

The reinforcement capability of fibres depends on the fibre properties, the interfacial bond between the fibre and the polymer matrix, and the critical fibre length [9]. The critical fibre length l_c is defined by fibre diameter d, fibre tensile strength σ_f^* and fibre–matrix bond strength τ_c, according to

$$l_c = \frac{\sigma_f^* d}{2\tau_c} \quad (1)$$

The equation indicates that the critical fibre length is proportional to the diameter of the fibre: the smaller the diameter is, the shorter the fibre can be still achieving reinforcement for the

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http://dx.doi.org/10.1016/j.compositesa.2014.02.002
1359-835X/

composite. Thus, the fibre dimensions can be referred as aspect ratio of the fibres: length of the fibre divided by fibre diameter (or fibre width), assuming that the fibre has a circular profile structure.

Wood fibres are sensitive to processing steps of thermoplastic natural fibre composites. Fibre length is reduced during compounding and moulding processes, and melt processing affects also the dispersion and orientation of the fibres in the polymer matrix. These changes are due to the high temperature and shear forces during processing. Shear forces in turn depend on the viscosity of the melt, which can be affected, e.g. by the polymer choice [10], the fibre and plasticizer content [11], and the compounding system [12].

The reinforcement capability of wood fibres in various matrix polymers has been studied earlier. Woodhams et al. [13] examined the effect of kraft pulp and thermomechanical pulp as fillers for polyolefins. Pulp fibres with dispersing agents improved the mechanical properties of polypropylene and polyethylene, and according to the authors, the produced pulp composites could offer significant cost and performance advantages compared to other construction materials. Migneault et al. [14] studied the effect of fibre length of birch chemithermomechanical pulp fibres on processing and properties using high density polyethylene as matrix. They found out that increasing fibre length had beneficial effects on mechanical properties of the composite. Maldas et al. [15] investigated the effect of different wood species on mechanical properties of polystyrene composites. They concluded that softwood pulps provide better reinforcement for the polymer than hardwood pulps, which is due to the differences in morphology, density and aspect ratios of the wood fibre types. Stark and Rowlands [1] compared the performance of various particle sized wood flours and refined wood fibres in polypropylene composites. As a result, the mechanical properties of the composites improved when wood fibres instead of wood flours were used. Polypropylene has been reinforced with cellulosic fibres also by Burgstaller et al. [16], concluding that pulp fibres are suitable for reinforcing polypropylene, showing high elastic modulus as well as high tensile strength. Ariño and Boldizar [17] studied the fibre breakage and mechanical properties of ethylene–acrylic acid copolymer and cellulose fibre composite, and according to their research, fibre length reduction during compounding was higher with longer fibres, and in most cases shorter fibres provided better fibre dispersion. The better dispersion was probably the reason why short fibres performed better than longer ones. The effect of processing on fibre length and dispersion in polypropylene–cellulose fibre composites has been investigated also by Baillif and Oksman [18]. The extrusion process resulted in fibre length reduction but the fibre diameter remained unchanged. Fibre dispersion was poor, probably due to hard and compact fibre pellets and lack of coupling agent. PLA has been reinforced with low aspect ratio wood fibres by Faludi et al. [19]. The study suggests that the interfacial adhesion between PLA and lignocellulosic fibres is strong by nature, having considerable specific interactions between the components. The use of short fibres resulted in decrease of tensile strength compared to neat polymer. In our recent research, long pine pulp and thermomechanical pulp fibres (TMP) fibres were compounded with PLA [20]. Wood fibres provided increased tensile and stiffness properties for PLA matrix. The improvement of mechanical properties was higher with TMP fibres, probably due to the higher stiffness of the fibres and better compatibility with PLA matrix.

In this study, two common polymers for WPC applications, polypropylene and bio-based PLA, were selected as comparable matrixes. Four types of wood fibres from paper industry were compared as reinforcement for the polymers. In addition to comparing the wood fibre types, also wood flour (conventional filler for wood plastic composites) was also used to compare the properties between fibres and particle-shaped flour. Additionally, chemical pulp fibres were dry-refined and compared to long pulp fibres. Fibre morphologies of the various fibre types were analysed before and after pilot-scale melt processing, which provides more information of the reinforcement capability of the fibres. Also the effect of the polymer type on the fibre morphology was detected by the fibre analysis. Viscosity measurements are presented to highlight the different melt characteristics of the compounds, which clearly have a distinct influence on the fibre cutting during melt processing. Fibre dispersion, mechanical properties and water absorption of the produced composites are compared to see the final effect of fibre type on the composite quality.

2. Experimental

2.1. Materials

2.1.1. Matrix

NatureWorks® polylactic acid (PLA) injection moulding grade 3051D and Borealis polypropylene (PP) injection moulding grade BG373MO were selected as matrix polymers of the composites. For improving the fibre/matrix adhesion between polypropylene and wood fibres, maleic anhydride grafted polypropylene (PP-MAH) granulates under the product name of Licomont AR 504 (Clariant GmbH) was used as a coupling agent.

The selected polymers have varying characteristics and properties. PLA 3051D is a transparent, semi-crystalline polymer made from bio-based raw material and intended for injection moulding applications. The melt flow index of this polymer is between 10 and 25 g/10 min. (210 °C/2.16 kg) [21]. PP BG373MO is a heterophasic, crystalline copolymer for applications such as pails and thin wall containers and can be processed with standard injection moulding techniques. The melt flow index of this PP grade is specified as 30 g/min (230 °C/2.16 kg) [22].

Some properties of the selected polymers can be seen from Table 1. Comparing the two polymers, PLA is stiff with higher stress at maximum load but relatively low impact strength, whereas PP is a more flexible material with moderate stiffness and higher ductility.

2.1.2. Fibres

Chemically bleached softwood kraft pulp made from pine and spruce (BSKP), bleached hardwood kraft pulps from eucalyptus (BHKP-e) and birch (BHKP-b), as well as thermomechanical (peroxide-bleached) spruce pulp (TMP) provided by UPM Kymmene were used in the experiments as wood fibres. The fibres were pelletised with a planar matrix pelletising machine (Amandus-Kahl) before compounding to enable adequate feeding into the compounder. In addition to pelletising process, BSKP fibres were refined as dry in Pallmann Machinenfabrik GmbH & Co. KG (Germany) (referred

Table 1
Glass transition temperature (T_g), melting point (T_m), Young's modulus (E), stress at maximum load (TS_{max}), impact strength (IS), and heat deflection temperature (HDT) of the matrix polymers.

Polymer	T_g (°C)	T_m (°C)	E (GPa)	TS_{max} (MPa)	IS (kJ/m^2)	HDT, 1.8 MPa (°C)
PLA 3051D	60	150–155	3.64 ± 0.03	61.5 ± 0.3	15.8 ± 0.6	52–53
PP BG373MO	–	165–170	1.60 ± 0.04	22.5 ± 0.2	65.5 ± 16.4	51–55

Table 2
Fibre characteristics of the pulp fibres after pelletising or refining (based on measurements with L&W STFI Fibermaster).

Measured properties	Unit	BSKP	BHKP-e	BHKP-b	TMP	BSKP-r
Fibre length[a]	mm	2.28	0.66	0.80	1.40	0.44
Fibre width[a]	μm	31.1	18.5	23.0	33.6	31.0
Aspect ratio	–	73	36	35	42	14.2
Fines content	%	8.6	9.1	7.4	27	37.3

[a] Length weighted average value.

Table 3
Wood flour characteristics.

Property	Unit	
Particle size mean	μm	728
Particle size median	μm	710
Particle size mode	μm	905
Particle size <50 μm	%	2.20
Particle size specific surface area	m^2/g	0.08

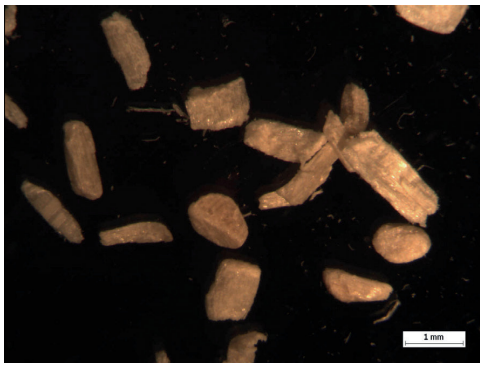

Fig. 1. Wood flour particles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as BSKP-r). Refining provides an optional method for fibre feeding in compounding process. Table 2 shows the fibre characteristics of pulp fibres after pelletising or refining.

Wood flour (WF) was obtained as a sawmill side stream. This pine/spruce wood flour had a mean particle size of 728 μm, other characteristics are given in Table 3. Fig. 1 shows the particle shape of wood flour, with low aspect ratio.

2.2. Biocomposite processing

Wood fibre pellets, dry refined fibres and wood flour were compounded with PP or PLA to a fibre content of 30 wt.% using a co-rotating twin-screw extruder (Berstorff ZE 25×33D). For production of polypropylene composites, PP-MAH was dry-mixed with PP granulates to total contents of 67 wt.% of PP and 3 wt.% of PP-MAH of the composite. The exact compositions of the produced composites can be seen from Table 4. Diameters and lengths of the screws of the twin-screw extruder were 25 mm and 870 mm respectively. To feed the materials, gravimetric side-feeders and a temperature gradient from 60 °C in the feeding section to 190 °C in the melting zones and the die and a screw speed of 200 rpm were used. All processing parameters are introduced in Table 5. After processing, the compounds were injection moulded with an injection-moulding machine (Engel ES 200/50 HL) into ISO 3167 tensile test specimens with a length of 150 mm and a 10 mm wide by 4 mm thick by 80 mm long mid-section. Also specimens from neat matrix polymers were produced as reference materials. After injection moulding, the tensile test specimens were kept in a room with standard conditions (23 °C, 50% relative humidity) for at least 5 days before testing.

Table 4
Sample codes and compositions of the produced composite and reference polymers.

Sample code	Polymer	Coupling agent	Fibre type	Polymer/coupling agent/fibre content (wt.%)
PLA-neat	PLA 3051D	–	–	100/0/0
PLA-30-BSKP	PLA 3051D	–	BSKP	70/0/30
PLA-30-BHKP-e	PLA 3051D	–	BHKP-e	70/0/30
PLA-30-BHKP-b	PLA 3051D	–	BHKP-b	70/0/30
PLA-30-TMP	PLA 3051D	–	TMP	70/0/30
PLA-30-WF	PLA 3051D	–	WF	70/0/30
PLA-30-BSKP-r	PLA3051D	–	BSKP-r	70/0/30
PP-neat	PP BG373MO	–	–	100/0/0
PP-30-BSKP	PP BG373MO	PP-MAH	BSKP	67/3/30
PP-30-BHKP-e	PP BG373MO	PP-MAH	BHKP-e	67/3/30
PP-30-BHKP-b	PP BG373MO	PP-MAH	BHKP-b	67/3/30
PP-30-TMP	PP BG373MO	PP-MAH	TMP	67/3/30
PP-30-WF	PP BG373MO	PP-MAH	WF	67/3/30
PP-30-BSKP-r	PP BG373MO	PP-MAH	BSKP-r	67/3/30

2.3. Characterisation

The produced composites were analysed with respect of fibre dispersion, water absorption, viscosity and mechanical properties. Also fibre dimensions after melt processing were investigated.

2.3.1. Fibre analysis

To determine the fibre properties after processing of the composites, the polymer matrix had to be dissolved from the injection moulded test specimen. In the PLA samples, the polymer matrix was dissolved with methylene chloride by heating the chemical to its boiling point (39.8 °C). The PP matrix was dissolved using xylene, heating the system in oil bath to 145 °C. The dissolved components were filtered in glass sinters and washed with the corresponding chemical. The dissolution procedure was repeated twice.

The dimensions of the remaining fibres were analysed using the automated fibre analyser L&W STFI FiberMaster. From the fibres, length, width, aspect ratio, and fines proportion were determined, including 2–3 reference measurements from each sample. Morphological features such as fibre structure or coverage with polymer after dissolving were characterised with the UV–VIS light microscope Olympus BX50, operating with single fibres suspended in deionised water. Partly, the fibres were stained with congored (1%-solution) in a short-time treatment. A fibre preparation was made from the diluted fibre–water suspension, and some drops of the congored solution were placed aside the cover glass and soaked carefully between object glass and cover glass. After 1 min reaction time, the fibres were rinsed between object glass and cover glass by adding few drops of pure water at the same position as previously the stain solution. These water drops were also soaked between object glass and cover glass, replacing the stain solution without flushing away the fibres. Adding water drops and soaking them through the preparation between object glass and cover glass was repeated until the water between the stained fibres was obviously clear. Both unstained and stained specimens were observed with UV-light in near violet range (wavelength 400–410 nm). Particle sizes of the wood flour were measured by UPM using the Coulter LS230 laser diffraction particle size analyser. Wood flour was suspended in water during measuring.

Table 5
Compounding process parameters.

Processing parameters	PLA-30-BSKP	PP-30-BSKP
Screw temp. Zone 2 (°C)	60	60
Screw temp. Zone 3–4 (°C)	140	140
Screw temp. Zone 5–9 (°C)	190	190
Screw speed (rpm)	200	200
Production rate (kg/h)	2.5	2.5
Back pressure (bar)	10	10
Torque (%)	55	30

2.3.2. Dispersion studies

The dispersion of the fibres in the matrix polymer was analysed both in macro- and micro-scale. For the macro-scale evaluation, macro pictures using a Canon Ixus 901S digital camera were taken, and the fibre agglomerates were estimated visually. For the micro-scale evaluation, thin microtome samples of the composite cross-sections were made and analysed using a Wild Heerbrugg M5A stereo microscope applying a magnification of 25×.

2.3.3. Water absorption tests

Water absorption tests were performed following the modified ISO-62 standard. For the tests, samples of the size 20 × 20 mm were cut from the head of the tensile test specimens and the cut cross sections were polished. From each compound, five reference samples were immersed in water and the samples were weighed after 24 h, 3 days, 1 week and 2 weeks of water immersion.

2.3.4. Viscosity measurements

Viscosity studies were performed using a capillary viscometer (Göttfert Rhaugraph 6000). Pure polymers were tested with a 1 mm nozzle in their maximum processing temperatures, and wood fibre filled materials with a 2 mm nozzle at temperature of 190 °C.

2.3.5. Tensile tests

Tensile properties were measured by an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA) with 10 kN load cell and a 5 mm/min cross-head speed at standard conditions (23 °C, 50%), applying the ISO 527 standard. Dumbbell samples with dimensions of about 4 mm thickness and 10 mm width were tested with a gauge length of 50 mm, grip distance of 115 mm and extensometer gauge of 50 mm. The dimensions of every specimen were measured with a slide calliper. Values of elastic modulus (GPa, linear regression between the strain of 0.0005 and 0.0025 mm/mm) and stress at maximum load (MPa) were determined from the average of five samples.

2.3.6. Impact strength

The impact strengths of the blends were determined using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy) according to ISO 179 standard with temperature of 23 °C and relative humidity of 50%. The tests were performed on unnotched specimens. Length, width, and thickness of the specimens were 80, 10 and 4 mm, respectively. Width and thickness of every specimen were determined by a slide gauge. Depending on the needed impact energy, 2 J or 4 J pendulums were used. The results were reported as impact energy (J) by the impact strength machine. The impact strength was then calculated using the information of impact energies and specimen dimensions according to Formula (2).

$$\text{Impact strength } (\text{kJ/m}^2) = \frac{\text{Impact energy (J)}}{\text{Width (mm)} \cdot \text{Thickness (mm)}} \cdot 1000 \quad (2)$$

3. Results and discussion

3.1. Apparent viscosity

Apparent viscosities of the neat PLA and PP together with composites containing 30 wt.% of BSKP fibres were measured to clarify the viscosity differences during processing (Fig. 2). A temperature of 190 °C was selected for the measurements to mimic the melt temperature of the polymers during the composite processing. As seen, PLA is more viscous in nature than PP. When fibres are added, the viscosities of the both compounds increase, PLA composite still being more viscous. More viscous nature of PLA compound indicates higher shear forces during melt processing compared to PP compound at the same temperature, which again correlates to higher fibre cutting. Thus, the viscosity results imply that fibre cutting is more extensive when PLA is used as matrix polymer instead of PP.

3.2. Fibre morphology

The best effect of interaction between fibre surface and polymer was seen in the light microscope using UV light with near violet filter (400–410 nm). The fluorescence effect caused either by the natural fibre wall components (auto-fluorescence) or by the polymer resulted in different colour appearance and intensity of the reflected light.

Fig. 3 shows pine fibres after dissolving of the polymer matrix in case of PLA and PP, compared to the reference fibres. Additionally to the visualisation of the interaction between auto-fluorescence and polymer fluorescence (images a, b, and c in Fig. 3), fibres were stained with congored (images d and e in Fig. 3).

The even colour of the fibres after dissolving of PP, turning from blue (reference, a) towards cyan (b) allows the conclusion that the polymer is not fully removed after the dissolving process but covering the fibre surface with a thin but even layer. Congored molecules cannot enter the pores of the fibre wall, subsequently these fibres appear unstained (d). Only in some points, where the coverage by polymer is disturbed, some stain molecules might migrate into the fibre wall pores, seen as slight reddish shine (arrows in d). The reason for the polymer remaining on the fibre surfaces lies in the use of coupling agent, which covalently bonds fibres to polymer.

PLA retains partly onto the fibre surface after the dissolving process. The fibre flexibility is reduced by the polymer, the fibres break down to shorter pieces in the blue polymer-free zones (arrows in c), whereas fibre parts with retained polymer (colour towards

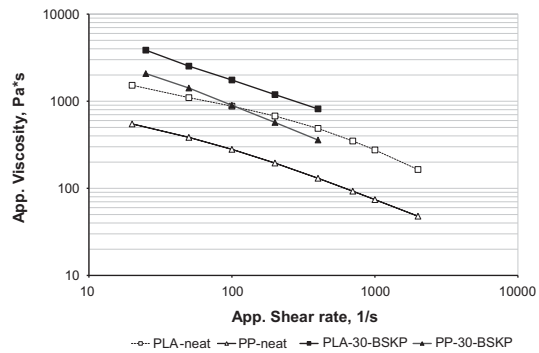

Fig. 2. Apparent viscosities of neat PLA and PP, and composites with 30 wt.% BSKP fibres, measured at 190 °C.

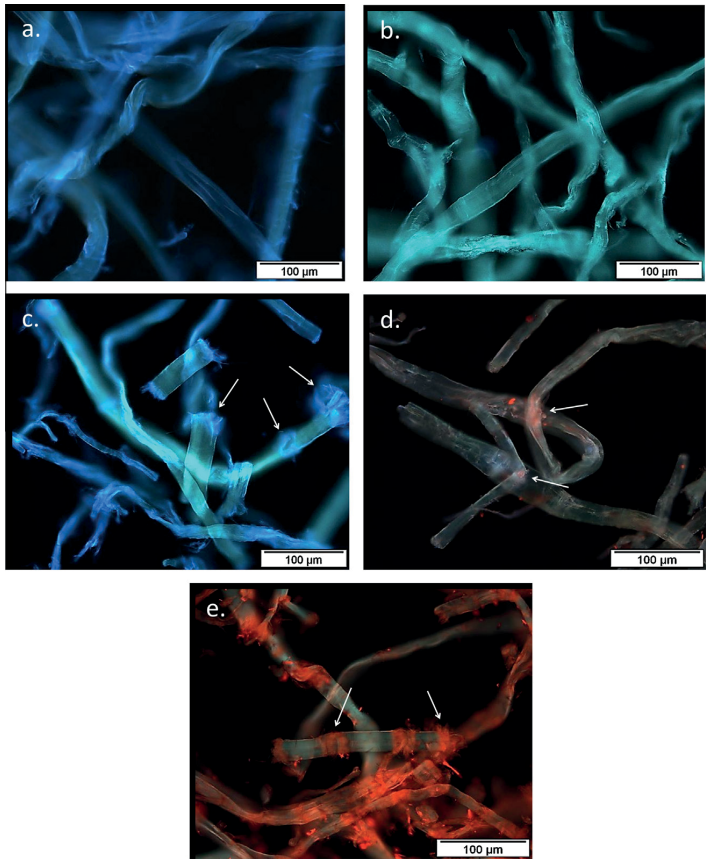

Fig. 3. BSKP fibres in UV-light (400–410 nm) after dissolving of the polymer matrix: (a) reference, (b) PP, (c) PLA, (d) PP stained with congored, (e) PLA stained with congored. Exposure times: 2500 ms (a, b and c), 1500 ms (d), and 1000 ms (e). *Arrows:* Zones with disturbed polymer cover (d), and polymer-free zones, where fibres can break (c and e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cyan) appear undeformed. This is also illustrated by the acceptance of congored molecules. The stain molecules migrate into the fibre wall from parts that are not covered with PLA anymore (arrows in e). Similar results were also found for the hardwood fibres.

From Fig. 3, also fibre destructions such as kinks can be observed, which might affect the reinforcement capability of the fibres in the polymer matrix. On the other hand, the remaining polymer on the fibre surface affects the collapsing of the fibre, and distorts the aspect ratio figures disabling their direct comparison to mechanical properties. The cutting of fibres after melt processing to PLA matrix is also obvious and discussed in the context of fibre dimension measurements (Fig. 4).

As shown in Table 2, within the selected chemically bleached pulp fibres from various origins, BSKP has the highest average fibre length compared to BHKP-E and BHKP-B: 2.28 mm in contrast to 0.66 and 0.80 mm, respectively. The corresponding values for TMP and dry-refined BSKP are 1.40 and 0.44 mm, respectively. Wood flour has an average particle size of 0.73 mm. Compounding of the fibres with polymer results in reduced fibre lengths, regardless of the fibre type or polymer matrix (Fig. 4). However, the longer the initial fibres are, the higher the reduction of fibre length after the melt processing seems to be, observed also by Ariño and Boldizar [17]. The fibre length reduction of BSKP fibres is vast in contrast to BHKP-E and BHKP-B, which have only slight reduction in length. In addition to the initial fibre length, the length decrease is also affected by the polymer matrix. It can be noticed that the decrease is higher with PLA matrix compared to PP due to the higher viscosity of the PLA melt during processing.

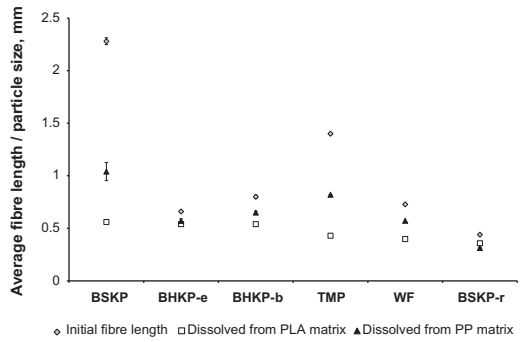

Fig. 4. Fibre lengths of wood fibre types before and after melt processing (compounding and injection moulding) with PLA or PP to fibre content of 30 wt.%.

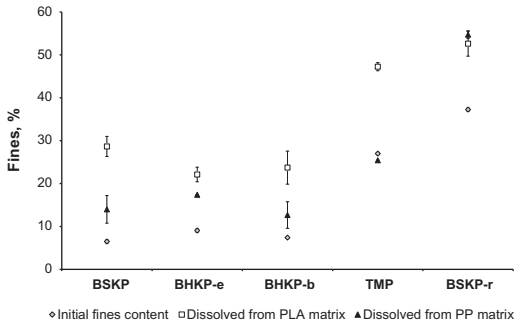

Fig. 5. Fine contents of different wood fibre types before and after melt processing (compounding and injection moulding) with PLA or PP to fibre content of 30 wt.%.

In PLA composites, fibre lengths are reduced to the same level due to the harsh processing conditions, independent of the fibre source and the initial fibre length. Therefore the aspect ratios of the fibres are only depended by the differences between widths of the original fibres: during melt processing, the fibres are cut only length-wise, fibre width preserving its dimension. The unchanged fibre diameter by extrusion process was also detected by Baillif and Oksman [18]. In the case of PP composites, shear forces during melt processing are lower, as discussed previously. Due to more gentle processing conditions, fibre cutting is lower and length differences between fibres from various fibre sources are preserved. Therefore, in PP composites, aspect ratios are depended on remaining lengths of the fibres as well as original fibre widths. However, as explained through microscopic analyses, the fibre width measurements and therefore also aspect ratio values are distorted because of the remaining PP in the surface of the fibres.

Melt processing also leads to increasing fines content in wood fibre reinforced composites (Fig. 5). Again, as the fibre cutting is more intense in PLA composites, higher amount of fine fibres is obtained. Specific data from fibre measurements are seen from Tables 6 and 7.

3.3. Fibre dispersion

The dispersion of the fibres from different origins in PLA and PP matrixes was visually observed in macro and micro-level. From the macro visualisation, it is noticed that while PLA composites containing BSKP and TMP fibres seem to be relatively uniform, some fibre agglomerates can be seen in eucalyptus and birch pulp composites (Fig. 6). On the other hand, the coarse quality of the wood flour is clearly visible. The colour of the TMP composite is darker because thermomechanical pulp contains lignin. In PP composites (Fig. 7), more fibre agglomerates are present and the fibre dispersion is clearly poorer than in the PLA matrix due to the lower melt viscosity of polypropylene and therefore lower shear forces during

Table 6
Fibre characteristics after melt processing dissolved from PLA matrix.

Fibre type	Fibre length (mm)	Length change[a] (%)	Fibre width (μm)	Width change[a] (%)	Aspect ratio (–)	AR change[a] (%)	Fines content (%)	Fines content change[a] (%)
BSKP	0.56	−75.4	30.1	−3.2	19	−74.0	28.7	233.7
BHKP-e	0.54	−18.2	17.9	−3.2	30	−16.7	22.1	142.9
BHKP-b	0.54	−32.5	21.4	−7.0	25	−28.6	23.7	220.3
TMP	0.43	−69.3	32.6	−3.0	13	−69.0	47.3	75.2
WF	0.40	−45.2	–	–	–	–	–	–
BSKP-r	0.36	−18.2	29.5	−5.5	12	−13.4	52.6	41.0

[a] Compared to original fibre measure.

Table 7
Fibre characteristics after melt processing dissolved from PP matrix.

Fibre type	Fibre length (mm)	Length change[a] (%)	Fibre width (μm)	Width change[a] (%)	Aspect ratio (–)	AR change[a] (%)	Fines content (%)	Fines content change[a] (%)
BSKP	1.04	−54.4	28.0	−10.0	37	−49.3	14.0	62.8
BHKP-e	0.57	−13.6	24.1	30.3	24	−33.3	17.4	91.2
BHKP-b	0.65	−18.8	26.6	15.7	24	−31.4	12.7	71.6
TMP	0.82	−41.4	35.4	5.4	23	−45.2	25.4	−5.9
WF	0.57	−21.9	–	–	–	–	–	–
BSKP-r	0.31	−29.5	29.2	−4.8	11	−26.1	54.7	46.6

[a] Compared to original fibre measure.

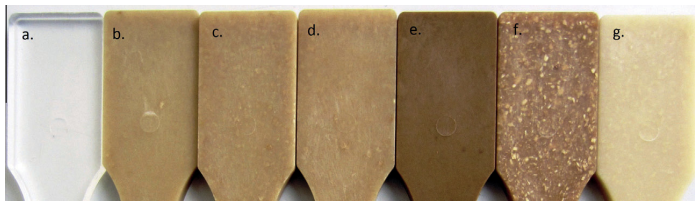

Fig. 6. Injection moulded tensile test specimen of PLA composites containing 30 wt.% of various wood fibre types. Fibres types in the composites from left to right: (a) neat polymer, (b) BSKP, (c) BHKP-e, (d) BHKP-b, (e) TMP, (f) WF, (g) BSKP-r. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

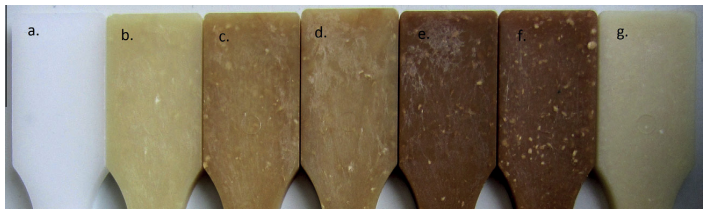

Fig. 7. Injection moulded tensile test specimen of PP composites containing 30 wt.% of various wood fibre types. Fibres types in the composites from left to right: (a) neat polymer, (b) BSKP, (c) BHKP-e, (d) BHKP-b, (e) TMP, (f) WF, (g) BSKP-r. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

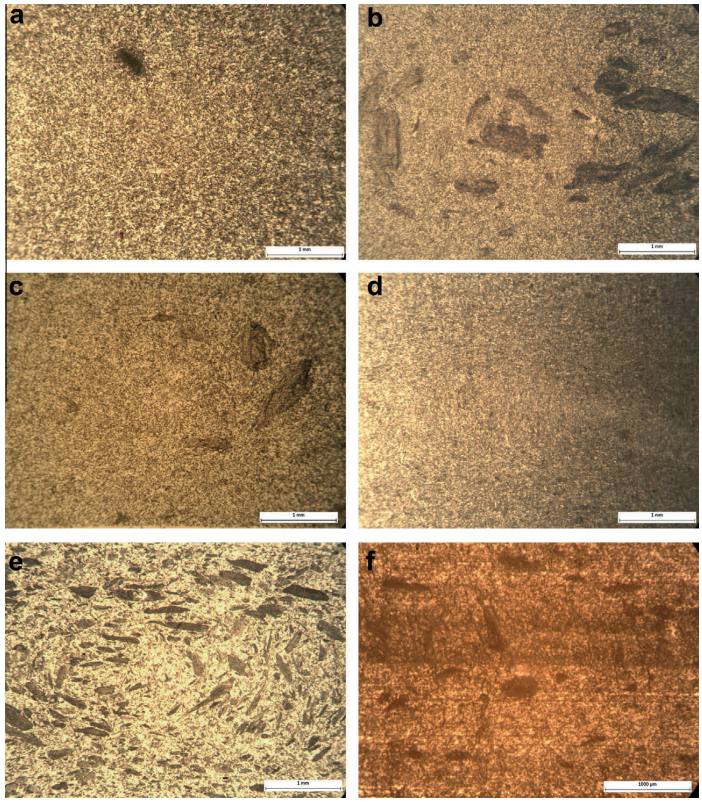

Fig. 8. Microscope pictures of PLA composite samples, magnification 25×. (a) PLA-30-BSKP, (b) PLA-30-BHKP-e, (c) PLA-30-BHKP-b, (d) PLA-30-TMP, (e) PLA-30-WF, (f) PLA-30-BSKP-r. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

melt processing, resulting in weaker breakage of the fibre pellets in the polymer melt.

The visual observations made in macro-level are affirmed by microscopic evaluations. As seen from Fig. 8, pelletised BSKP (b) and TMP (d) fibres have a very uniform dispersion in the PLA matrix, whereas some agglomerates exists with BHKP-e (b) and BHKP-b (c). In the PLA composite containing wood flour (e), the various particle sizes and shapes of the flour are visible. Dry-refined BSKP fibres (e) have formed agglomerates, and the fibres are not dispersed well in PLA matrix.

Again, the fibre dispersion in the PP matrix is inferior to PLA composites due to the weaker break-up of the fibre pellets during melt processing. When comparing the various wood fibre composites (Fig. 9), the least agglomerates are found in BSKP reinforced polypropylene (a). TMP fibres (d) are not dispersing as well in the PP matrix as in PLA polymer. Similarly to PLA composites, wood flour (e) is detected as larger particles, and dry-refined BSKP (f) have created fibre agglomerates.

3.4. Water absorption

Differences in water absorption of various samples can be detected after the water immersion of the neat polymers and composites (Table 8). Polypropylene has more hydrophobic characteristics than PLA and absorbs therefore less water. The addition of a wood based component to the polymer evidently affects the water absorption due to its hydrophilicity and by creating a network of fibres through which the water can diffuse inside the

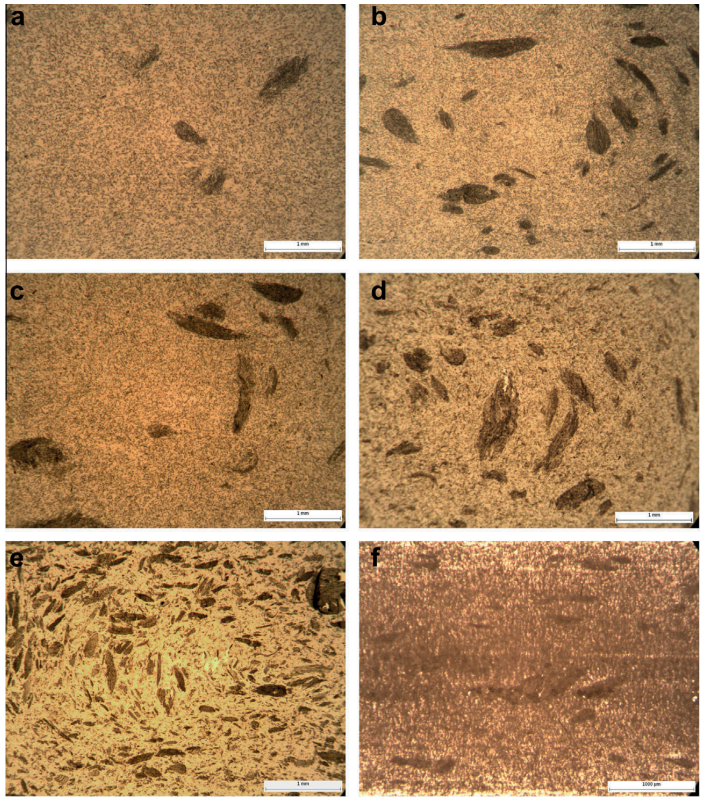

Fig. 9. Microscope pictures of PP composite samples, magnification 25×. (a) PP-30-BSKP, (b) PP-30-BHKP-e, (c) PP-30-BHKP-b, (d) PP-30-TMP, (e) PP-30-WF, (f) PP-30-BSKP-r. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 8
Weight changes of the produced composites after 24 h, 3 days, 1 week, and 2 weeks of water immersion.

Sample code	24 h (%)	3 days (%)	1 week (%)	2 weeks (%)
PLA-neat	0.30 ± 0.04	0.48 ± 0.02	0.62 ± 0.05	0.71 ± 0.03
PLA-30-BSKP	0.73 ± 0.07	1.48 ± 0.03	2.12 ± 0.06	3.10 ± 0.15
PLA-30-BHKP-e	1.03 ± 0.02	2.26 ± 0.15	2.94 ± 0.06	4.17 ± 0.07
PLA-30-BHKP-b	0.87 ± 0.04	2.00 ± 0.05	2.64 ± 0.06	3.72 ± 0.05
PLA-30-TMP	0.77 ± 0.05	1.69 ± 0.02	2.41 ± 0.06	3.69 ± 0.07
PLA-30-WF	1.03 ± 0.04	2.13 ± 0.10	2.97 ± 0.08	4.29 ± 0.15
PP-neat	0.05 ± 0.05	0.34 ± 0.14	0.33 ± 0.06	0.38 ± 0.06
PP-30-BSKP	0.38 ± 0.08	0.72 ± 0.07	1.01 ± 0.05	1.37 ± 0.10
PP-30-BHKP-e	0.42 ± 0.03	0.91 ± 0.10	1.29 ± 0.09	1.92 ± 0.10
PP-30-BHKP-b	0.51 ± 0.14	0.88 ± 0.05	1.33 ± 0.09	1.88 ± 0.14
PP-30-TMP	0.66 ± 0.04	1.48 ± 0.07	1.79 ± 0.12	2.57 ± 0.10
PP-30-WF	0.40 ± 0.03	0.82 ± 0.10	1.07 ± 0.04	1.46 ± 0.11

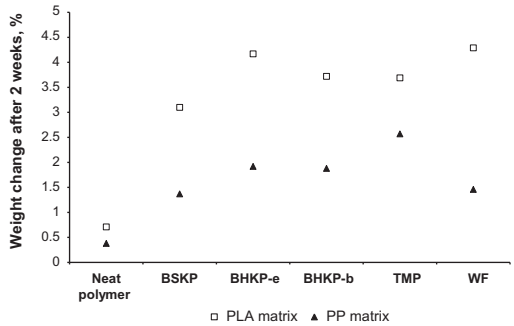

Fig. 10. Water absorption of PLA and PP composites after 2 weeks.

sample. The results show a correlation with fibre dispersion studies, suggesting that a good fibre dispersion leads to reduced water absorption levels. Thus, the lowest water absorption of both PLA and PP composites is found when BSKP fibres have been used as reinforcement (Fig. 10). The more agglomerates are visible, the higher is the water absorption. Fibre agglomerates lead to an inconsistent material with possible cracks and voids, which results in more efficient water absorption. On the other hand, even though the fibre dispersion of TMP fibres in the PLA matrix is uniform and suggest a good water repellence, still the water is absorbed in a greater amount compared to BSKP. This could be due to the clearly higher fines content of the TMP composite, creating a continuous fibre network through the sample for the water to be absorbed.

3.5. Mechanical properties

Mechanical properties (Young's modulus, maximum tensile strength and impact strength) of the produced composites were analysed and compared. In Fig. 11, Young's modulus values have been normalised with respect to matrix polymers to see the relative change of the corresponding property. As a result, the addition

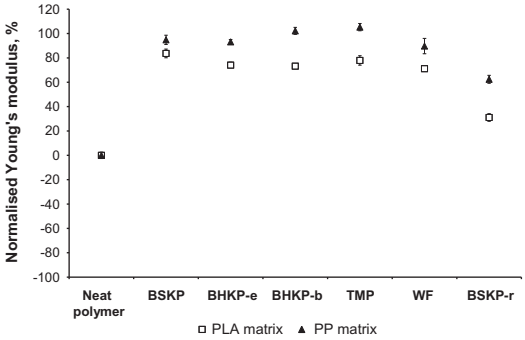

Fig. 11. Young's modulus of 30 wt.% wood fibre composites normalised with respect to the matrix polymers of the composites.

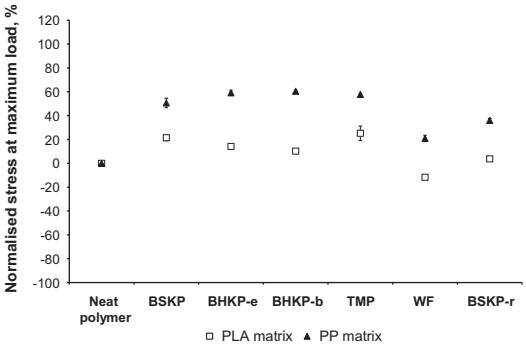

Fig. 12. Stress at maximum load of 30 wt.% wood fibre composites normalised with respect to the matrix polymers of the composites.

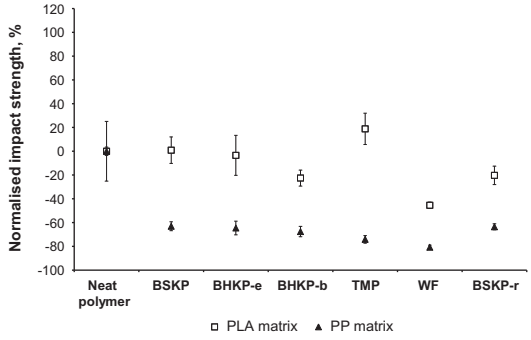

Fig. 13. Impact strengths of 30 wt.% wood fibre composites normalised with respect to the matrix polymers of the composites.

Table 9
Mechanical properties of the wood fibre composite compounds.

Sample code	Tensile strength (MPa)	Elastic modulus (GPa)	Impact strength (kJ/m^2)
PLA-neat	61.5 ± 0.3	3.64 ± 0.03	15.9 ± 0.6
PLA-30-BSKP	74.7 ± 1.6	6.69 ± 0.13	16.1 ± 1.8
PLA-30-BHKP-e	70.2 ± 0.5	6.34 ± 0.09	15.4 ± 2.7
PLA-30-BHKP-b	67.8 ± 0.6	6.31 ± 0.07	12.3 ± 1.1
PLA-30-TMP	77.0 ± 3.7	6.48 ± 0.14	18.9 ± 2.1
PLA-30-WF	54.3 ± 1.1	6.23 ± 0.05	8.7 ± 0.4
PLA-30-BSKP-r	63.8 ± 0.5	4.77 ± 0.11	12.7 ± 1.2
PP-neat	22.5 ± 0.2	1.60 ± 0.04	65.5 ± 16.4
PP-30-BSKP	33.9 ± 0.9	3.12 ± 0.06	24.2 ± 2.5
PP-30-BHKP-e	35.8 ± 0.5	3.09 ± 0.03	23.2 ± 3.8
PP-30-BHKP-b	36.1 ± 0.2	3.24 ± 0.05	21.2 ± 2.9
PP-30-TMP	35.5 ± 0.1	3.28 ± 0.05	17.0 ± 2.1
PP-30-WF	27.2 ± 0.6	3.04 ± 0.10	12.6 ± 1.2
PP-30-BSKP-r	30.6 ± 0.3	2.56 ± 0.05	23.9 ± 1.6

of wood components to PLA and PP polymers increases the stiffness of the polymers. The effect is somewhat stronger with the polypropylene matrix, which has lower initial stiffness characteristics. In general, wood fibres lead to a higher stiffness than wood flour or dry-refined fibres, the latter performing clearly the weakest. In PLA composites, BSKP fibres provide the best performance, and in the case of PP, the highest stiffness values are obtained when TMP fibres are used.

The relative strength differences of the produced composites with respect to neat matrix polymers can be seen from Fig. 12. For both matrix types, wood flour performs the weakest: in the case of PLA, the strength of the wood flour composite is even lower than without wood particles, indicating that wood flour is not acting as reinforcement, but as filler in PLA composites. On the other hand, all the pulp fibre types have a clear reinforcing effect for PLA, from which TMP is giving the highest value. The reason for high mechanical properties of TMP fibres might be the fact that TMP fibres are stiffer than chemically bleached fibres. It is also suggested that hydrophobic lignin in TMP fibres might act as a compatibiliser between the PLA polymer and the fibres, thus improving the fibre–matrix adhesion [23]. When chemical pulp fibres in PLA matrix are compared, the highest strength is attained by BSKP fibres. This is probably due to the better fibre dispersion of BSKP fibres compared to BHKP-E, BHKP-B or BSKP-r fibres in the PLA matrix, leading to a more homogenous structure, in which the internal stresses are divided more evenly. For PP composites, a slight reinforcement effect is obtained by using wood flour, but pulp fibres provide clearly higher tensile properties. The differences between the pulp fibre types are minor except the BSKP-r, strength of which is lower than the other fibres.

Due to the different natures of the two selected polymers, the effect of pulp fibre reinforcement on the impact strengths of the material differs (Fig. 13). PLA has a ductility value of 15.8 kJ/m^2 on its own. The well dispersed BSKP fibres sustain the ductility of the material at the same level, and TMP fibres increase the impact strength by 19%. This supports the claim of lignin improving the fibre/matrix interface in wood fibre/PLA composites. The poorer fibre dispersions of eucalyptus and birch pulp and dry-refined fibres seem to have a negative effect on the impact strength. Again, wood flour performs the weakest, decreasing the impact strength significantly. On the other hand, polypropylene being a ductile material is suffering from the addition of wood fibres or wood flour with clearly decreased impact strength values. The largest decrease results from the use of wood flour. TMP fibres are also performing worse than chemically bleached fibres. Data of the mechanical properties of all the produced composite samples are seen in Table 9.

4. Conclusions

– Length reduction and increase in fines content of wood fibres during melt processing steps is higher with longer BSKP fibres than with shorter hardwood types. Lower shear forces during melt processing of PP composites results in

lower fibre cutting than in processing of PLA composites. With PLA, the average fibre lengths are at the same level after processing irrespective of the fibre type.

- After separation of fibres from the polymer matrix by dissolving technique, some of the polymer is still remaining on the fibres either as thin films, or covering the fibres partly, affecting the collapsing of the fibres and thus width dimensions. Subsequently, the measured aspect ratios of the fibres after melt processing are distorted (especially in the PP matrix), and cannot directly be compared to mechanical properties of the composites. The observed fibre destructions such as kinks might affect the reinforcement capability of the fibre in the polymer matrix.
- The fibres disperse better to PLA matrix than to PP, leading to more effective breakage of the fibre pellets and dispersion of individual fibres during compounding. The best dispersion was achieved with BSKP and TMP fibres in PLA matrix. Wood flour remains as large particles in both polymer matrixes. Dry-refined BSKP fibres create fibre agglomerates, resulting in poor fibre dispersion.
- TMP fibres provide the best performance in PLA composites with the highest tensile strength and impact strength properties compared to other fibre types. Wood flour acts as filler, not as reinforcement for the polymer.
- In contrast to wood fibres, wood flour is not reinforcing PP matrix, resulting in clearly weaker mechanical properties than fibre form. Stiffness and tensile strength are improved with all wood fibres, but impact strength is decreased compared to neat PP. The deviation in the performance of various wood fibres is lower than in PLA based composites.
- Aspect ratio values of the fibres after melt processing cannot be compared with the ductility properties of the composites due to the distorted fibre width measurements affected by the remaining polymer on the fibre surfaces. Also, fibres are not dispersed equally between various fibre types, so no straight conclusions between aspect ratio and mechanical performance of the composites can be made.
- Dry-refining of wood fibres is not a promising alternative for fibre feeding. Refined fibres lose their reinforcing capability and have tendency to agglomeration, resulting in lower mechanical properties of composites compared to pelletised wood fibres.

Acknowledgements

The research leading to these results received funding from the European Community's Seventh Framework Programme (FP7-NMP-2007-LARGE-1) under grant agreement number 214714. The authors are grateful to UPM Kymmene for supplying the pulps and performing particle size analysis of the wood flour.

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PUBLICATION III

Effects of physical treatment of wood fibres on fibre morphology and biocomposite properties

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Plastics, Rubber and Composites 40 (2) (2011), 86-92
https://doi.org/10.1179/174328911X12988622801016

Effects of physical treatment of wood fibres on fibre morphology and biocomposite properties

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In the study, the effect of refining and fractionation of wood fibres on fibre morphology and biocomposite properties was determined. Kraft pine pulp and thermomechanical pulp were selected for the fibre treatments. Effects of physical treatment on fibre morphology were analysed with a fibre analyser and microscopy techniques. For the composites, polylactic acid was used as a polymer matrix. Composites were produced by melt processing to a fibre content of 30 wt-%, and the mechanical properties of the injection moulded biocomposites were investigated. In general, thermomechanical pulp fibres improved the mechanical properties of polylactic acid more than pine pulp fibres did. Two different fibre fractions with distinct fibre properties were obtained by fractionation, and the use of a long fibre fraction provided improved mechanical properties for composites. The refining of pine pulp led to clear fibrillation of the fibre surface, but it had a negative effect on the mechanical properties of biocomposites.

Keywords: WPC, Biocomposites, Wood fibres, Refining, Fractionation

This paper is part of a special issue on manufacturing and design of composites

Introduction

In conventional wood plastic composites (WPCs), sawdust or wood powder is usually used as a filler for polyolefins. For reinforced plastic applications, increasing interest in the use of wood fibres instead of wood powders can be detected.[1–3] To enable the full reinforcement capacity of wood based fibres, problems such as insufficient fibre dispersion and adhesion to the matrix, inconsistent fibre uniformity and durability during processing have to be solved. To overcome these obstacles, options such as physical, chemical or enzymatic fibre treatments can be studied. In papermaking, two common physical treatments for wood fibres are fractionation and refining.

Fibre fractionation is a process in which pulp fibres are sorted based on their physical properties, and the resulting fibre fractions can have significantly different fibre properties. Today, there are two main industrial scale devices used to fractionate pulp fibres: pressure screens and hydrocyclones. In pressure screens, the sorting of fibres is based on the dimensional properties (length and width) of the fibres, whereas in hydrocyclones it is mainly based on the density and specific surface area (fibre surface area per gram) of the fibres.[4] Many other parameters than those related to fibre morphology also affect the efficiency of fractionation and the quality of fractions. General overviews of these methods can be found in the references.[5,6]

Refining of pulp is known to increase the strength properties of paper.[7] The bonding capacity of the fibres is improved by increasing the formability and the bonding surface area of the fibres. Refining is also known to affect fibres in many other ways. The most important effects are external fibrillation, fines production, length reduction and internal changes in the wall structure. Refined fibres are therefore more collapsed (flattened), fibrillated and flexible than unrefined fibres.[7] In addition, McIntosh and Uhrig[8] have found that refining does not greatly decrease the tensile strength of a single fibre.

This study looks at the effects of refining and dimensional based fractionation on fibre morphology and the mechanical properties of WPCs. Refining increases the surface area of the fibres, which can lead to better fibre–matrix adhesion in composite applications. Fractioning, on the other hand, offers a great opportunity to affect fibre material uniformity and the possibility of using longer fibres with more reinforcing potential.

Experimental

Fibre treatments

Chemically bleached kraft pine pulp and thermomechanically ground (peroxide bleached) spruce pulp provided by UPM Kymmene were used in the experiments. Fractionation of the thermomechanical pulp (TMP) was performed using the Metso FS-03 laboratory screen type sorter. After fractionation, thick A4 sheets were prepared and cut into chads by a paper shredder device before compounding. Pine pulp was refined by the Escher Wyss laboratory refiner LR1. The fibres were pelletised with a planar

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Published by Maney on behalf of the Institute
Received 16 July 2010; accepted 5 October 2010
DOI 10.1179/174328911X12988622801016

matrix pelletising machine (Amandus-Kahl) before compounding.

Biocomposite processing

NatureWorks polylactic acid (PLA) injection moulding grades 3001D and 3051D were used as matrix polymers of biocomposites. Physically treated fibres were compounded with PLA to a fibre content of 30 wt-% using a co-rotating twin screw extruder (Berstorff ZE 25 × 33D). The diameters and lengths of the screws were 25 and 870 mm respectively. To feed the materials, gravimetric side feeders were used. A temperature gradient from 60°C in the feeding section to 190°C in the melting zones and the die, and a screw speed of 200 rev min^{-1} were used. After processing, the compounds were injection moulded with an injection moulding machine (Engel ES 200/50 HL) into ISO 3167 tensile test specimens with a length of 150 mm and a 10 mm wide by 4 mm thick by 80 mm long centre section. After injection moulding, the tensile test specimens were kept in a room with standard conditions (23°C, 50% relative humidity) for at least five days before testing.

Measurements

The fibre dimension measurements were performed using the L&W STFI FiberMaster device. The total amount of lignin in the TMP fractions was determined by the Klason lignin method. Light microscope imaging of fibres was performed with a Nikon Eclipse ME600 device. The charge coupled device camera used was the PCO SensiCam LongExposure. Photos were taken at ×50 or ×100 magnification. Wet fibres were stained with methylene blue colour.

Laboratory paper sheets were prepared using the SCAN-C 26 : 76 standard, and the tensile index of paper was determined using the SCAN-P 38 : 80 standard. The refining level of pulp was analysed using the Canadian standard freeness (CSF) measurement (SCAN-C 21 : 6). The ISO 527 and ISO 179 standards were used in the mechanical testing of the composite specimens. To determine the fibre lengths of the injection moulded specimens, the PLA matrix was dissolved with chloroform and the remaining fibres were analysed with the L&W STFI FiberMaster device.

Table 1 Fibre dimension measurements of TMP and kraft pine pulp

Measured properties	Initial TMP	Initial pine pulp
Fibre length*/mm	1·39	2·37
Fibre width*/μm	34	30
Aspect ratio	41	78
Fines/%	27	6·89
Lignin content/%	26	<0·20

*Length weighted values (measured using a FiberMaster device). The fibre properties were measured from the pulp.

Results and discussion

Fibre morphology

Reference pulps

Untreated TMP and chemically bleached kraft pine pulp were selected as reference pulps, and their initial fibre properties were measured from pulp before any treatments.

Thermomechanical pulp and chemically bleached pine pulp differ in many ways (Table 1). The amount of lignin in TMP is high, whereas bleached pine pulp is almost lignin free. Thermomechanical pulp contains clearly more fines than kraft pine pulp, and TMP fibres are shorter and have a lower aspect ratio than pine pulp fibres. In the literature, mechanical pulp fibres are described as stiffer, coarser and straighter than chemical pulp fibres.[9]

Fractionation

Thermomechanical pulp was fractionated by fibre dimensions into short and long fractions in nine sorting steps. The fibre properties were measured from rewetted chads and the results are shown in Table 2. Preparation of the sheets and shredding them into chads affected the fibre properties of the reference fibres slightly, and the results of the fibre measurements therefore differ from the initial fibre values (Table 1).

Two fractions with different fibre dimensions were obtained by fractionation. The fibre length and width of the long fraction were clearly higher than those of the short fraction, and thus the aspect ratio of the long fraction was also higher. The short fraction also had a higher fines content. As is known from the literature, fines have a large surface area, which improves bonding between fibres.[9] Consequently, the tensile strength of the paper from the short fraction was a bit higher than that from the long fraction.

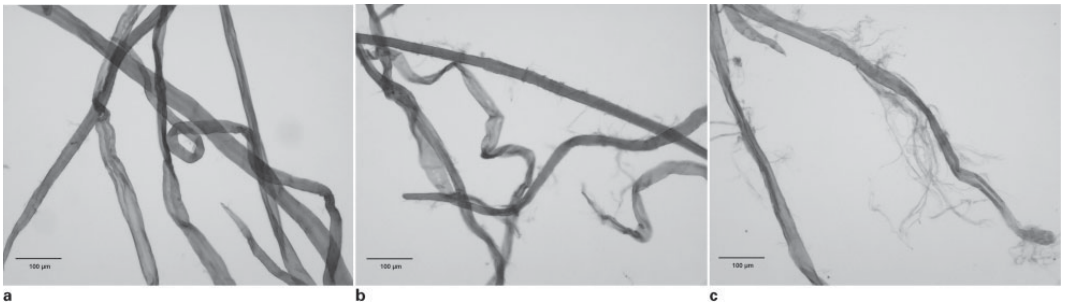
In addition to the effect on fibre morphology, the lignin content of the TMP fractions was also influenced by fractionation. The short fraction of TMP had a higher lignin content than the reference and the long fraction fibres because fine particles include more lignin than long fibres.[10]

Long fibres and a high aspect ratio of fibres are expected to lead to better mechanical properties of composites than short fibres because the composite strength and stiffness are directly proportional to the length and diameter of the reinforcing fibre.[11] The long fibre fraction produced with decreased fines content should therefore provide increased composite properties.

Table 2 Fibre dimension measurements and pulp properties of different fractions of TMP

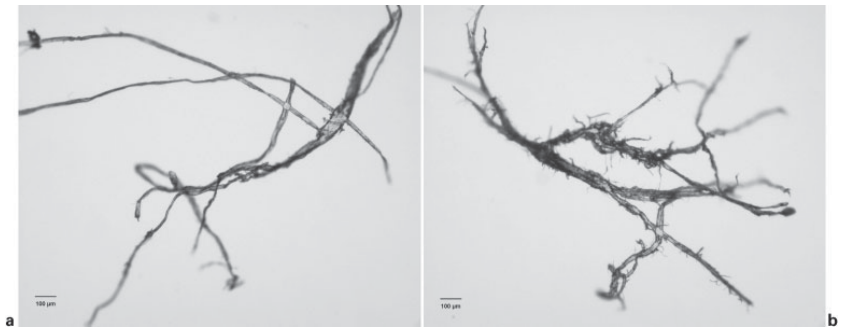
Measured properties	Unfractioned TMP	Short fraction of TMP	Long fraction of TMP
CSF/mL	80	<10	240
Fibre length*/mm	1·11	0·74	1·23
Fibre width*/μm	34	29	34
Aspect ratio	33	26	37
Fines/%	27	47	20
Lignin content/%	26	30	24
Tensile index of paper/Nm g^{-1}	44	47	41

*Length weighted values (measured using a FiberMaster device). The fibre properties were measured from the rewetted shredded sheets before compounding.



a unrefined fibres; *b* 120 kWh t^{-1} refined fibres; *c* 200 kWh t^{-1} refined fibres

1 Light microscope images from wet and stained pine pulp fibres at ×100 magnification



a unrefined fibres; *b* 200 kWh t^{-1} refined fibres

2 Light microscope images from dry pine pulp fibres at ×50 magnification

Refining

Chemically bleached pine pulp was refined at two levels with refining energies of 120 and 200 kWh t^{-1}. The pelletising process influenced fibre properties. The measured values in Table 3 therefore differ from the initial values of the chemical pine fibres (Table 1).

Table 3 shows that reasonable refining of pine pulp fibres did not affect fibre dimensions significantly. The fines content of the pulp increased during refining and even doubled at a refining level of 200 kWh t^{-1}. As the bonding capacity and the fines content of the fibres were increased by refining the pulp, the tensile index of the laboratory sheets was increased radically.

The effects of refining on the fibre surface can be seen clearly from the light microscope images (Figs. 1 and 2). Figure 1 was taken in the wet state from fibres of rewetted pellets and Fig. 2 in the dry state from the fibres pulled out from dry pellets.

It can be seen that the surface of the unrefined pine pulp fibres was intact and that there is no external fibrillation on the fibres (Fig. 1*a*). Figure 1*b* and *c* shows that strong external fibrillation of refined fibres exists. It is said that external fibrillation exists only in water suspension and that the removal of water brings external fibrils back to the fibre surface.[9] Figure 2, however, shows that there is a clear difference between the dried unrefined and refined fibres. The surface of the refined fibres is much rougher than that of the unrefined fibres.

By increasing the surface area of the fibres, the adhesion between the fibre and polymer might be expected to improve. Improved mechanical properties of composites may be obtained through better fibre–matrix adhesion.

Biocomposite properties

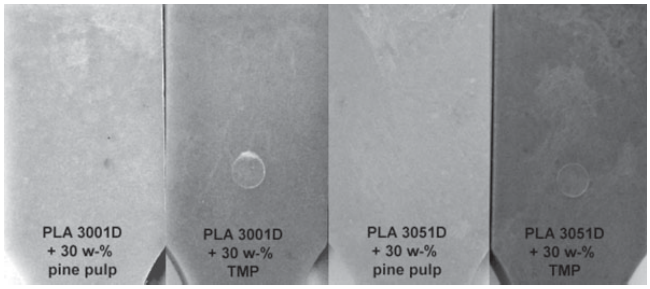
Reference composites

Reference composites with untreated TMP and chemically bleached kraft pine pulp fibres and two grades of

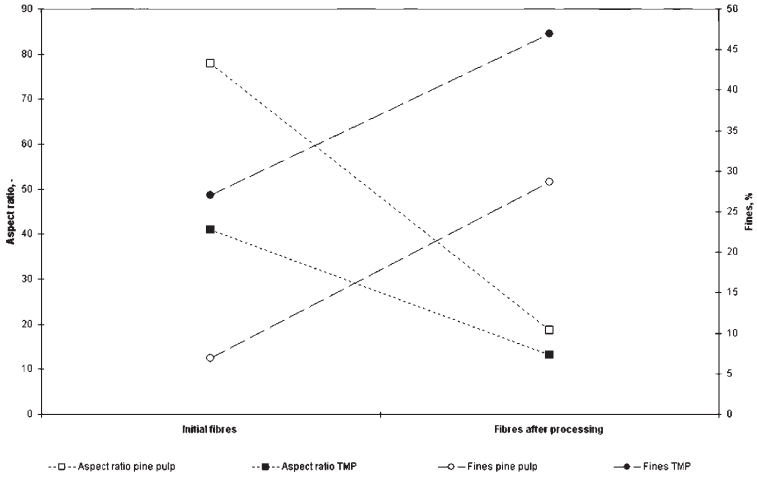
Table 3 Fibre dimension measurements and pulp properties of unrefined and refined pine pulps

Measured properties	Unrefined pine pulp	Refining level 1	Refining level 2
Specific energy consumption/kWh t^{-1}	0	120	200
CSF/mL	680	570	390
Fibre length*/mm	2·17	2·10	2·02
Fibre width*/μm	31	31	32
Aspect ratio	70	67	63
Fines/%	6·50	9·50	13
Tensile index of paper/Nm g^{-1}	36	59	66

*Length weighted values (measured using a FiberMaster device). The fibre properties were measured from rewetted pellets.



3 Colour differences of pine pulp and TMP composites depending on PLA grade matrix



4 Effect of processing (compounding and injection moulding) on aspect ratios and fines contents of pine pulp and TMP fibres: to measure fibres after processing, PLA 3051D matrix was dissolved from injection moulded specimen and remaining fibres were analysed

PLA were produced according to the method described earlier. Table 4 summarises some of the primary properties of the two PLA grades used in the study. The clearest difference between the two PLA injection moulding grades is the melt flow index: PLA 3051D is more viscous compared with PLA 3001D at the same melting temperatures.

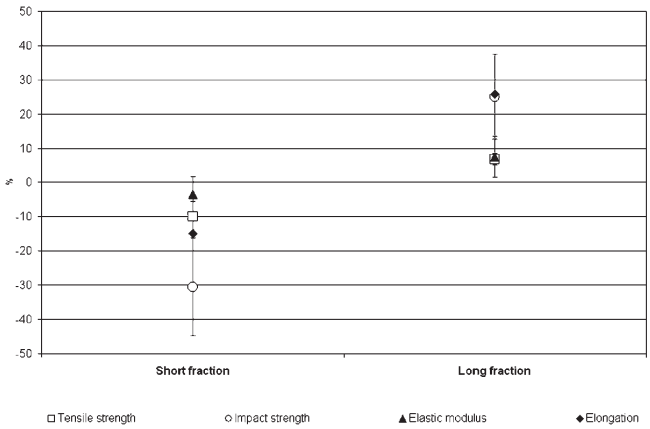
Figure 3 represents colour differences between the composites with 30 wt-% fibres using the same processing conditions when two different PLA grades are used. As can be seen, samples with PLA 3051D are darker than PLA 3001D specimens. This is due to the higher shear forces that exist during processing, which in turn depend on the higher viscosity of PLA 3051D. This

Table 4 Some properties of NatureWorks PLA grades[12]

Grade	Specific gravity	Melt flow index/g (10 min)$^{-1}$	Melt temperature/°C
PLA 3001D	1·24	10–30 (190°C, 2·16 kg)	200
PLA 3051D	1·25	10–25 (210°C, 2·16 kg)	200

Table 5 Mechanical properties of pure PLAs and composites with 30 wt-% fibres

Polymer	Fibre	Fibre form	Polymer/ fibre/wt-%	Tensile strength/MPa	Elastic modulus/GPa	Impact strength/kJ m^{-2}	Elongation/%
PLA 3001D	…	…	100/0	65·1±0·5	3·601±0·045	18·2±0·4	3·0±0·2
PLA 3001D	Pine pulp	Chad	70/30	67·8±1·3	6·190±0·053	15·5±2·0	1·6±0·1
PLA 3001D	TMP	Chad	70/30	75·2±1·2	6·192±0·376	14·9±1·9	1·7±0·2
PLA 3051D	…	…	100/0	61·5±0·3	3·640±0·032	15·8±0·6	4·9±0·6
PLA 3051D	Pine pulp	Pellets	70/30	71·6±0·5	6·375±0·086	16·1±3·7	2·1±0·2
PLA 3051D	TMP	Pellets	70/30	77·0±3·7	6·476±0·140	18·9±2·1	1·8±0·3

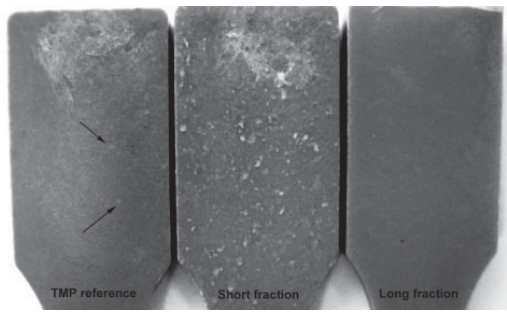


5 Effect of fractionation of TMP fibres on mechanical properties of PLA composites containing 30 wt-% fibres: results are normalised with respect to composites containing TMP reference fibres (no fractioning)

again leads to increased pressure and temperature at the processing step, inducing discolouration of the temperature sensitive wood fibres. The use of TMP fibres leads to a darker colour than chemically bleached (lignin removed) pine pulp, as the lignin containing TMP fibres are yellowish by nature.

The mechanical properties of the neat PLAs and reference composites can be seen from Table 5. The addition of 30 wt-% fibres increased the elastic modulus, or stiffness, of both PLAs dramatically. The tensile strength also increased, whereas the elongation decreased. The ductility (or impact strength) of PLA 3001D was slightly reduced when fibres were added, though the fibre addition increased the ductility of PLA 3051D.

When comparing the fibre types in PLA composites, TMP fibres showed better mechanical properties than pine pulp fibres in general, with only a few exceptions. This was the case although the higher aspect ratio and the lower fines content of the initial pine pulp fibres could have offered better reinforcement for composite applications. There are some explanations for TMP fibres providing better mechanical properties for PLA composites than pine pulp. The advantage of the higher aspect ratio of pine pulp fibres was actually lost in the processing step (Fig. 4). The shear forces during compounding and injection moulding led to extensive fibre cutting, as longer fibres are more susceptible to length reduction than shorter fibres or fines. Full processing of the composites resulted in a greater length reduction of the pine pulp fibres, leading to almost the same aspect ratio as fully processed TMP fibres. With the aspect ratios at the same level, the reason for the higher composite mechanical properties might be that TMP fibres are stiffer than chemically bleached pine pulp fibres. On the other hand, the lignin in TMP fibres might act as an adhesion promoter between the PLA polymer and the fibres, thus improving fibre–matrix adhesion.[13] With its hydrophobic nature, lignin can act as a compatibilizer between the hydrophilic fibres and the hydrophobic matrix polymer, thus strengthening the fibre/matrix interface and leading to improved composite properties.



6 Macroscale fibre dispersion of unfractioned and fractioned (short and long fractions) TMP fibres in PLA matrix with fibre content of 30 wt-%

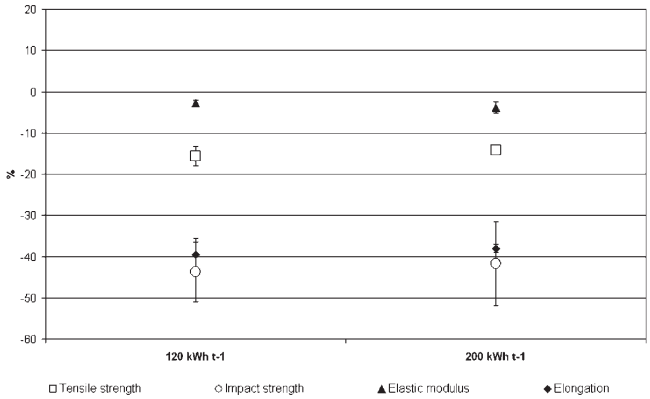
Fractionation

Two fractions of TMP fibres (short and long fractions) were compounded with PLA 3001D, and the mechanical properties of the composites were studied. The results can be seen in Table 6.

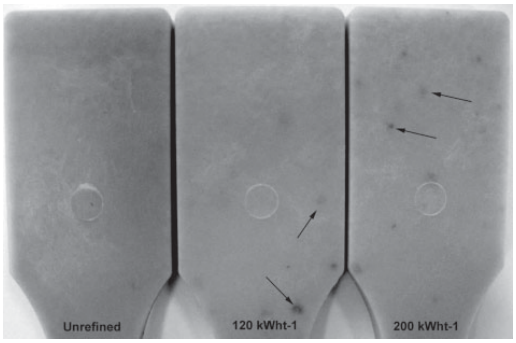
The influence of the use of short and long fibre fractions with respect to the TMP reference (untreated) fibres is represented in Fig. 5. The fractionation of TMP had a clear effect on the mechanical properties of the composites. The use of the short fibre fraction in PLA composites led to reduced mechanical properties: tensile strength 10%, impact strength 30%, elastic modulus 3% and elongation 15%. The long fibre fraction, however, provided improved composite mechanical properties

Table 6 Effect of fractioning on mechanical properties of PLA 3001D/TMP composites

PLA/pine/wt-%	Fibre fraction	Tensile strength/MPa	Elastic modulus/GPa	Impact strength/kJ m^{-2}	Elongation/%
70/30	Unfractioned	75·2±1·2	6·192±0·376	14·9±1·9	1·7±0·2
70/30	Short	67·7±3·3	5·982±0·316	10·4±2·1	1·5±0·2
70/30	Long	80·3±1·2	6·652±0·369	18·7±1·9	2·2±0·3



7 Effect of refining pine pulp fibres on mechanical properties of PLA composites containing 30 wt-% fibres: results are normalised with respect to composite containing pine pulp reference fibres (no refining)



8 Macroscale fibre dispersion of unrefined and refined pine pulp fibres in PLA matrix with fibre content of 30 wt-%

with improvements in the tensile strength of 7%, impact strength 25%, elastic modulus 7% and elongation 26%. By removing the fines from the TMP, longer, more uniform fibres were obtained that provided a better reinforcement capability. The bonding capability of the longer fibres was also weaker, which probably led to better fibre dispersion and thus greater reinforcement of the polymer. The improved fibre dispersion of the composites with a long fibre fraction and reduced fibre dispersion with a short fibre fraction can be seen in Fig. 6, where clear agglomerates can be observed in the short fraction case.

Refining

Pine pulp fibres refined into levels (120 and 200 kWh t^{-1}) were compounded with PLA 3051D, and the mechanical properties of the specimens were measured (Table 7).

The effect of fibre refining on the mechanical properties of composites with unrefined pine pulp fibres can be seen in Fig. 7. The refining of the fibres led to a decrease in composite properties, although the fibrils in the fibre surface could have improved the adhesion between the fibres and matrix polymer. The reduction is due to the increased fines content, which leads to a decreased fibre reinforcement capability of very short fibres as well as fibre dispersion, the latter of which is due to the stronger bonding capability of short fibres. The effect of refining on fibre dispersion can be seen in Fig. 8, in which the poor fibre dispersion of the samples containing refined fibres can be detected from the visible fibre agglomerates.

Conclusions

Two different kinds of pulp were chosen for the study: TMP and chemically bleached kraft pine pulp. Thermomechanical pulp contains lignin, which is removed from bleached pine pulp during the pulping process. In addition, TMP fibres are shorter, stiffer and have a lower aspect ratio than chemical pulp fibres. In PLA composites, TMP fibres showed better mechanical properties in general than chemically bleached kraft pine pulp fibres. The higher aspect ratio of pine pulp fibres was lost in the composite processing step, leading to aspect ratios of the same level for both fibres. Consequently, the better mechanical properties of TMP may be due to the higher stiffness of the fibres. In addition, lignin in TMP fibres may act as a compatibilizer between the fibres and PLA polymer, thus improving fibre–matrix adhesion.

The fractionation of TMP fibres led to two distinct fibre fractions with different fibre properties. The longer fibre length, the higher aspect ratio and the lower fines content of the long fibre fraction offered a higher reinforcement capability for WPCs, thus clearly improving the mechanical properties of the produced biocomposites. The lower

Table 7 Effect of refining on mechanical properties of PLA 3051D/pine pulp composites

PLA/pine/wt-%	Refining	Tensile strength/MPa	Elastic modulus/MPa	Impact strength/kJ m^{-2}	Elongation/%
70/30	Unrefined	71·6±0·5	6·375±0·086	16·1±3·7	2·1±0·2
70/30	120 kWh t^{-1}	60·4±1·7	6·200±0·039	9·1±1·17	1·2±0·1
70/30	200 kWh t^{-1}	61·4±0·3	6·131±0·088	9·4±1·63	1·3±0·0

fines content and more uniform fibres in the long fibre fraction improved the dispersion of the fibres in the polymer matrix, whereas the poor fibre dispersion in the short fibre fraction composites containing more fines could clearly be detected.

The refining of kraft pulp fibres showed clear fibrillation of the fibre surfaces. This led to an increase in the surface area of the fibres, thus improving the fibre bonding and tensile properties of the paper. However, the refining did not give any benefits in composite manufacturing. The use of unrefined pine pulp fibres in composite applications gave better WPC mechanical properties than refined fibres did, and the distribution of fibres was also better. One reason for this is that the refined fibres formed very strong bonds between the fibres, and the pellets made from these were too tough to be able to open up and disperse well in the polymer melt during the compounding step. The refined fibres therefore remained as agglomerates rather than single fibres, and fibre dispersion decreased. The use of chemicals that weaken the fibre–fibre bonds before pelletising can improve this situation. The fines content increased when the pulp was refined, providing another explanation as to why the mechanical properties of the composites and the fibre dispersion suffered.

Acknowledgements

The research leading to these results received funding from the European Community's Seventh Framework Programme (FP7-NMP-2007-LARGE-1) under grant agreement no. 214714. The authors are grateful to UPM Kymmene for supplying the pulps and measuring the lignin content of the TMP fractions.

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PUBLICATION IV

Recycled fibres and fibrous sludge as reinforcement materials in injection moulded polypropylene (PP) and poly(lactic acid) (PLA) composites

Pääkkönen, Elina; Wikström, Lisa; Peltola, Heidi; Valta, Kyösti; Retulainen, Elias

Journal of Bioresources and Bioproducts 2(3) (2017), 116-122
http://dx.doi.org/10.21967/jbb.v2i3.140

Journal of Bioresources and Bioproducts. 2017, 2(3): 116-122 *Peer-Reviewed*

ORIGINAL PAPER

Recycled fibres and fibrous sludge as reinforcement materials in injection moulded polypropylene (PP) and poly(lactic acid) (PLA) composites

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ABSTRACT

Wood flour or sawdust is often used as filler in conventional wood plastic composite (WPC) materials. However, there has been an increasing interest to the use of wood pulp fibres in reinforced plastic applications, because they can provide enhanced strength properties and better biodegradability characteristics for the composite. This research compares the effect of recycled fibres or side streams of paper as reinforcement in poly(lactic acid) (PLA) or polypropylene (PP) composites. Fibres from liquid packaging board and non-deinked old newspapers, and fibrous sludge from recycling processes are compared with virgin softwood kraft pulp fibres. Composites were produced by melt processing to a fibre content of 30% (or 10% fibrous sludge), and the mechanical properties were investigated. Recycled fibres provided comparable, or even higher, plastic reinforcement than virgin softwood fibres. In PP composites, the differences in mechanical properties between different fibre types were relatively small. Fibrous sludge decreased the mechanical performance of composites but can be considered as cheap filler in cases when mechanical properties are not crucial. The possibility to use low-cost materials like recovered paper or deinking sludge in wood plastic composites is an interesting option for future sustainable applications.

Keywords: Wood fibres; Liquid packaging board; Fibrous sludge; Recycled fibres; Biocomposite; Mechanical properties

1. INTRODUCTION

Usually wood flour or sawdust is used as filler in conventional wood plastic composite materials. However, there is also an increasing interest towards the use of wood pulp fibres, either from hardwood or softwood origin, in reinforced plastic applications, because they can provide enhanced strength properties in addition to reduction of raw material cost and improvement of the biodegradability characteristics of the composites.

To have the strengthening function, the reinforcing fibre materials should have a high length/diameter ratio and good adhesion to the polymer matrix.[1-4] The typical length of softwood pulp fibres is above 2 mm, and hardwood fibres around 1 mm. However, during melt processing the fibres tend to be cut down to a length of 0.5 mm or shorter.[5,6] Fibres with a low aspect ratio cannot provide improved impact strength, even if other mechanical properties are increased.[7] Problems in adhesion are mostly due to the hydrophilic nature of wood-based materials, which decreases their compatibility with hydrophobic polymers. Hydrophilic fibres also make the composite material more susceptible to moisture.[8] In addition to fibre dimensions and fibre-matrix adhesion, fibres should also be well dispersed and distributed to the matrix polymer for optimal mechanical performance.[6,9]

The possibility to use low-cost materials like recovered paper or deinking sludge in WPCs is an interesting option for future sustainable applications. For this, recovered paper can be pulped and de-inked, but using non-deinked pulp would be a simpler and more attractive approach. This is especially interesting because the disintegration and de-fibring of some paper grades in papermaking lines presents inherent difficulties due to the lack of suitable treatment systems or due to polyethylene coating, hydrophobic or wet strength chemicals, etc. In that case the recovered material as such or after a minor sorting or screening operations contains, in addition to cellulosic fibres, also chemicals (wax, wet strength agents, and release agents), ink, adhesives and mineral pigments. This raises an interesting question: what is the effect of these residuals on composite performance?

In Europe the utilization rate of recycled fibres in newsprint is about 90%,[10] which already has a negative effect on end product quality. Virgin fibre-based newsprint is typically made of mechanical pulp, but recycled fibre-based newsprint contains also fillers, and mechanical and chemical pulp fibres from old magazines (OMG) in addition to old newspapers (ONP). For improving water holdout in the printing process also hydrophobic sizing agents may be added to furnish. Typically newspapers are printed using the coldset web offset printing method and oil-based inks that are relatively easy to remove in the deinking process. However, also flexographic printing processes are used which are known to have very poor deinkability. The water-based colors dissolve in the

deinking process contaminating the whole batch. The critical amount of flexo-printed recycled paper in the deinking process is estimated to be about 3%.[11] The best way to solve this problem is to sort out the flexo-printed papers before the deinking process. This material could be used in composites. There are a few previous studies regarding the use of ONP fibres in thermoplastic composite applications. For example, Serrano et al. replaced glass fibres with old newspaper recycled fibres as reinforcement in PP matrix.[12] The mechanical performance of the old newspaper reinforced PP was supposed to be reasonable for, e.g. some structural products. Huda et al. studied recycled newspaper fibre in PLA and PP matrixes and compared the performance of these composites to PLA/talc and PP/talc composites[13,14] and also to glass-fibre composites.[15] The results showed that recycled fibres are a good alternative as reinforcement for biocomposites. Both mechanical and thermo-physical properties of ONP-reinforced PLA composites could be comparable with glass fibre-reinforced PLA composites, although the impact strength decreased slightly. Bhardwaj et al. noticed that the addition of 40 wt% recycled fibres to polyhydroxybutyrate-co-valerate (PHBV) -based composites improved the tensile and storage moduli clearly.[16] On the other hand, also in this case, the impact strength decreased with the increasing amount of recycled fibres both in PHBV- and PP composites.

Liquid packaging board (LPB) is used for packaging of fresh milk products and juice. The board is coated with polyethylene on both sides, and the base board consists typically of three layers made of virgin fibre material. The top and back layers are made of bleached kraft pulp, and the middle layer made of mechanical or chemithermomechanical pulp (CTMP) and/or bleached or unbleached kraft pulp. In order to reduce raw edge wicking of liquid into the board, the material is strongly sized and therefore hydrophobic. Longer shelf life products contain also an aluminium foil layer. The fibre material is recyclable and can be separated from the polyethylene and aluminium layer.[17] Because of the purity and hygienic requirements the fibre material cannot be re-used in food packaging but in making lower quality board. However, due to the lack of collection and suitable recovery systems in many areas the fibre material may end up being used in energy production. An interesting option would be to use the material in composite production.

In pulp and paper mills, especially in the deinking process, some fibrous sludge is formed. There is a need for finding valuable applications for this material instead of landfilling. A few scientific papers have focused on using sludge as a filler in composites.[18-23] The key driver is to reduce waste disposal costs that can be high and will rise further in the future, and the main interest is in retaining mechanical properties on an acceptable level. In wood plastic composites, replacing 10% of wood particles with 10% of paper sludge was found to give basically similar mechanical properties.[21] The maximum operational filler content seemed to be about 10%; beyond that, the reduction of strength properties occurs rapidly. The potential applications are, for example, massive composite items like pallets and other construction engineering products.

In this study, various fibre side streams and recycled fibres are utilized as reinforcement material in WPC applications. In contrast to previous studies, the research will provide wider perspective on the reinforcement capability of the various recycled fibre types, as the effect of fibres are systematically compared to each other and also to virgin softwood kraft pulp, which is already used in commercial wood fibre composite materials. In addition, fibres are applied to and compared in two typical WPC polymer matrixes, polypropylene and poly(lactic acid), giving wider outlook on the general material properties. The selected fibres (liquid packaging board, old newspapers and fibrous sludge) were pre-treated the same way (pelletised) before compounding for fair comparison. WPC samples were produced by melt processing to a fibre content of 30 wt% or fibrous sludge content of 10 wt%, and the mechanical properties, visual appearance and compatibility of the injection molded specimens were determined and compared in terms of fibre type and matrix polymer.

2. EXPERIMENTAL

2.1 Materials

Fibres

Four different kinds of fibrous material obtained from the paper industry were used in the experiments: virgin bleached softwood kraft pulp (BSKP), old newspaper fibres (ONP), liquid packaging board fibres (LPB), and fibrous sludge. Dry virgin bleached chemical softwood kraft pulp from the Kaukas pulp mill and fibrous sludge (~59% solid content) from the Kaipola recycled pulp mill were provided by UPM Kymmene. The fibrous sludge consisted of 60% inorganic material, about 40% organic material and material from the flotation deinking, the screening rejects of the recycling process, and other paper mill reject streams. Non-deinked old newspaper was obtained by pulping local newspapers. The local newspaper was produced from recycled fibres and printed by using the cold-set offset process. Newspapers contain normally less than 15% of filler. LPB without PE-coating was supplied by Stora Enso. The board consisted of three layers: top and bottom plies made of solid bleached sulfate pulps and the middle ply made mainly of mechanical pulp like CTMP but containing also some BSKP. The board was sized with hydrophobic and/or wet strength sizes to reduce liquid absorption and improve wet strength.

Matrix polymers

Injection molding grade 3051D PLA from NatureWorks® and PP grade BG373MO from Borealis

were used as matrix polymers for the wood plastic composites. For improving the fibre/matrix adhesion between hydrophobic PP matrix and the hydrophilic wood fibres, maleic anhydride grafted PP was used as a coupling agent.

2.2 Processing

Fibre pre-treatments

Bleached softwood kraft pulp sheets, old newspapers and liquid packaging board sheets (without PE coating) were slushed (the fibrous sludge was already wet) and each of them were pelletised with a planar matrix pelletising machine before compounding to enable adequate feeding into the compounder. This type of pelletising process had only a slight effect on the fibre dimensions. The pellets were dried in an oven.

Composite processing

Pelletised wood fibres were compounded with PLA and PP polymers to a fibre content of 30% or sludge content of 10% by using a co-rotating twin-screw extruder (ZE 25×48D, Berstorff GmbH, Hannover, Germany). Temperature <190 °C and a screw speed of 200 1/min were used for both PLA and PP compounds. The exact compositions and sample codes of the produced compounds are seen in Table 1.

Table 1 Sample codes and compositions of the produced composites and reference polymers.

Sample code Polymer-fibre	Fibre type	Polymer/ coupling agent/ fibre content (wt.%)
PLA	-	100/0/0
PLA-BSKP	BSKP	70/0/30
PLA-LPB	LPB	70/0/30
PLA-ONP	ONP	70/0/30
PLA-ONP/Fibrous sludge	ONP/Fibrous sludge	70/0/20/10
PLA-Fibrous sludge	Fibrous sludge	70/0/10
PP	-	100/0/0
PP-BSKP	BSKP	67/3/30
PP-LPB	LPB	67/3/30
PP-ONP	ONP	67/3/30
PP-ONP/Fibrous sludge	ONP/Fibrous sludge	67/3/20/10
PP-Fibrous sludge	Fibrous sludge	87/3/10

The compounds were injection molded with an injection-molding machine (Engel ES 200/50 HL, Engel Austria GmbH, Schwertberg, Austria) into ISO 3167 tensile test specimen.

2.3 Characterization

Fibre and paper analysis

Fibre properties were analysed by using the L&W STFI FiberMaster device (ISO/DIS 16065-2 standard) before pelletisation. Laboratory sheets (60 g/m^2) were prepared using the SCAN-C 26:76 standard and sheets were dried and stored at least four hours in an air-conditioned laboratory room (23 °C, RH 50%) before analysis. Hand sheets from the mixture of fibrous sludge (33%) and recycled fibres (66%) were made by using extra fabric on the wire to improve the drainage of smaller particles. Hand sheets from pure fibrous sludge were not prepared because of the negligible strength due to the high amount of inert fine particles and inorganic material. The contact angle, θ, of water droplets on the paper sheet surface was measured by using a CAM200 contact angle meter. Ash content of the pulps was determined at 500 °C (SCAN-P 5:63) to avoid decomposition of the possible carbonate filler component.

Tensile and impact tests

The ISO-527 and ISO-179 standards were used in the mechanical testing of the specimens. Tensile tests were performed using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA) with a 10 kN load cell and a 5 mm/min cross-head speed. Impact strengths were determined by using a Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy). Impact strength tests were performed on unnotched specimens. The test specimens were kept in standard conditions (23 °C, 50% relative humidity) for at least five days before testing.

A JEOL JSM-6360LV microscope was used for SEM-analysis of the composites. Fracture surfaces of tensile or impact test specimens were qualitatively investigated to evaluate the compatibility between the PP or PLA matrix and the fibres.

3. RESULTS AND DISCUSSION

3.1 Fibre and paper properties

Fibre properties of the pulps were analyzed before the processing phase and can be seen from Table 2. BSKP showed the highest average fibre length (2.29 mm) compared to other pulps. The average fibre length values for LPB, ONP and the mixture of ONP fibres and fibrous sludge were 1.72 mm, 1.37 mm and 1.03 mm, respectively. Fines content of the pulps were 7.1% for BSKP, 11.2% for LPB, 26.7% for ONP and 34.7% for the ONP/Fibrous sludge -mixture. Fibre properties of pure fibrous sludge were not analysed because it included a large amount of small non-fibrous and inorganic particles that cannot be detected by a fibre analyser. Ash content was determined at

500 °C from ONP and fibrous sludge. ONP pulp contained 11.2% ash and the fibrous sludge 46.4%.

Table 2 Analysed fibre characteristics

Fibre code	Fibre length (mm)	Aspect ratio (-)	Fines content (%)
BSKP	2.29	76.4	7.1
LPB	1.72	52.6	11.2
ONP	1.37	43.1	26.7
ONP/Fibrous sludge	1.03	38.0	34.7
Fibrous sludge	n.d.	n.d.	n.d.

n.d. not determined

Contact angle values of water drops on the paper surface can give us a better understanding of the hydrophobic or hydrophilic nature of fibres. Low values indicate that water spreads well and wets the paper, while high values indicate poor wetting. Figure 1 shows the contact angles for water drops as a function of time. Softwood kraft pulp sheets had low contact angle values and water drops were rapidly absorbed. LPB sheets showed the highest contact angle values and longest absorption time period, indicating that the fibres are clearly more hydrophobic than softwood kraft pulp fibres. This can be explained by sizing made for LPB to reduce liquid absorption. ONP and a mixture of ONP and fibrous sludge sheets also showed high contact angles, but water was absorbed more quickly than with LPB sheets.

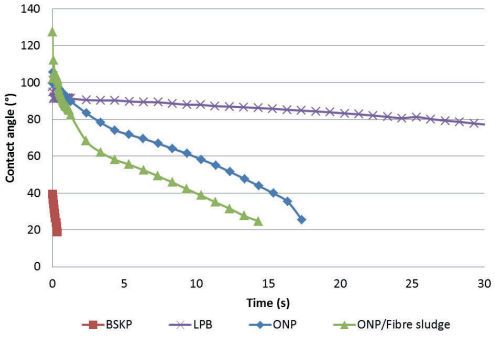


Fig. 1. Contact angle values for water drops on the surface of paper sheets. Contact angle values are the mean value of three measurements.

3.2 Composite properties

Mechanical performance

Both PLA and PP compounds were compounded with a twin-screw extruder, injection molded and tested according to methods described earlier. Mechanical properties of the produced PLA composites are presented in Figure 2 and PP composites in Figure 3. The addition of 30% of virgin kraft pulp fibres and recycled fibres to PLA and PP improved both tensile strength and modulus values of both polymers. The effect of cellulosic fibres on the modulus is also known from the literature.[13, 24] However, it is interesting that the recycled fibres perform in both PLA and PP matrixes as well as or even better than the reference virgin pulp fibres (BSKP) when tensile strength and modulus are concerned. However, the good impact strength (ductility) of neat PP was reduced notably when fibres were added, regardless of the fibre source. The impact strength of neat PLA stayed on the same level or was slightly increased with 30% fibre addition. The same trend was seen in a previous study in which PLA was reinforced with thermomechanical pulp (TMP) and bleached pine kraft pulp.[24] Even if the impact strength has been seen as a weak point of natural fibre-reinforced biocomposites,[25] the wood fibre reinforcement, also recycled fibres, are able to maintain the impact strength of PLA and at the same time increase both modulus and impact strength.

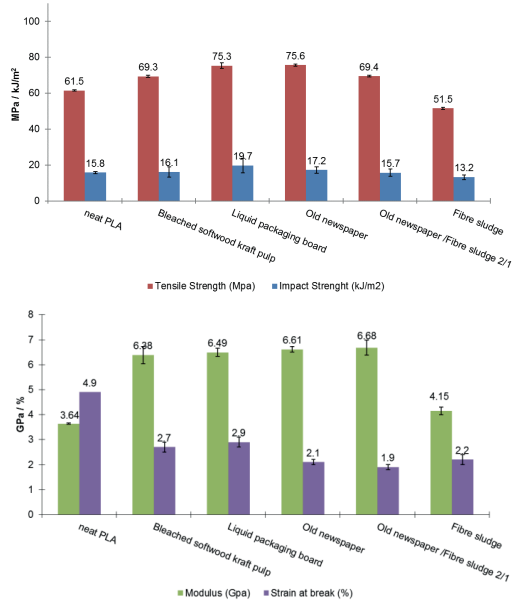
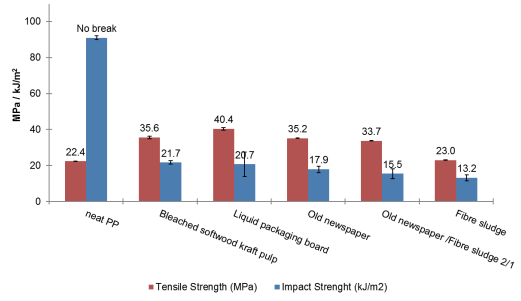


Fig. 2. Mechanical properties of PLA matrix and PLA composites with 30 or 10 wt-% of fibres.



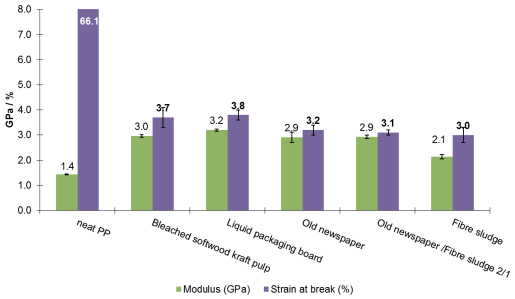


Fig. 3. Mechanical properties of PP matrix and PP composites with 30 or 10% of fibres.

When fibre types are compared, the LPB fibres showed the overall best performance with both polymer matrixes. Our previous study[6] showed that thermomechanical pulp fibres in PLA give better mechanical properties than BSKP fibres. This was assumed to be due to the stiffer characteristics or higher lignin content of TMP fibres. It has been suggested that lignin in the fibres could act as an adhesion promoter thus improving fibre-matrix adhesion.[26,24] The fines content of ONP is higher than of LPB, leading to a lower amount of reinforcing fibres in the composite. In addition, LPB fibres have higher hydrophobicity due to the hydrophobic resins added in the board making process, even if the water contact angles showed that the hydrophobicity of the sheets was only slightly higher than that of ONP sheets. On the other hand, the high contact angle of ONP sheets can be due to oil-based printing inks rather than hydrophobic fibres. Possibly the combination of high hydrophobicity and longer fibres may be the reason for the good strengthening ability of LPB fibres.

Addition of 10% fibrous sludge increases the modulus of neat PP and PLA from 1.4 GPa to 2.1 GPa with PP and from 3.6 GPa to 4.2 GPa with PLA while tensile strength stays at the same level with PP and weakens with PLA. Fibrous sludge contains 60% of inorganic material which might affect the compatibility of the fibrous sludge and the polymer. In general, fibrous sludge affects the mechanical properties of the composites the same way as wood flour,[6] thus it could be regarded as very low cost filler that has the ability to improve composite stiffness.

Visual appearance

The color of the prepared samples varied from yellowish to dark brown (Figure 4 and Figure 5). BSKP is almost lignin-free and gives a light color to the composites. LPB contains also some lignin-containing mechanical pulp, which leads to a bit darker color. ONP pulp as well as fibrous sludge in the experiments contains a lot of inks from the newspapers, which gives the composites a dark brown color. The light color of the composites containing BSKP and LPB makes it possible to color them using plastic colorants during compounding or injection molding. On the other hand, inks can be removed from recycled fibres by the deinking process so a lighter color of the ONP composites would be attainable.

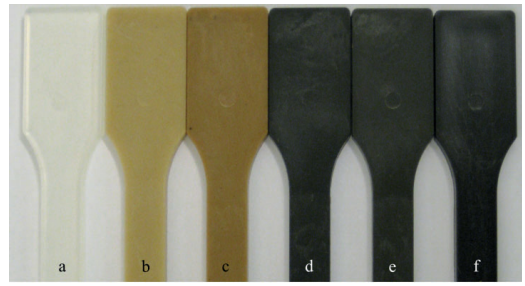


Fig. 4 Visual appearance of the poly(lactic acid) -based samples: a) PLA; b) PLA-BSKP; c) PLA-LPB; d) PLA-ONP; e) PLA-ONP/Fibrous sludge; f) PLA-Fibrous sludge

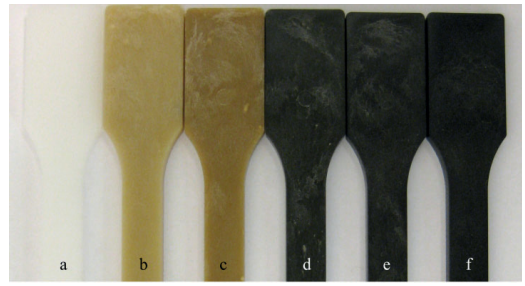


Fig. 5 Visual appearance of the polypropylene -based samples: a) PP; b) PP-BSKP; c) PP-LPB; d) PP-ONP; e) PP-ONP/Fibrous sludge; f) PP-Fibrous sludge

Compatibility

Scanning electron spectroscopy (SEM) was employed to analyse the compatibility of the fibres and polymer of the samples. Test specimens of injection molded neat PLA and PLA–fibre composites, obtained after tensile testing, are shown in Figure 6. Several small holes with diameter <20 µm were visible on the fracture surface of the PLA-softwood kraft pulp test specimen (Figure 6b). It seemed that there were less fibre pull-outs in samples with other fibres (LPB, ONP and fibrous sludge). Higher hydrophobicity of the LPB, ONP and fibrous sludge probably improved PLA matrix-fibre interaction. Broken fibres were observed in all samples. Although the matrix-fibre interaction according to the SEM images seemed to be weaker with softwood kraft pulp in the PLA matrix than with the other fibres; the mechanical properties of the composites were only a bit lower than with LPB and ONP. The longer fibres and higher aspect ratio of softwood

kraft pulp fibres probably compensates the weaknesses in the matrix-fibre adhesion.

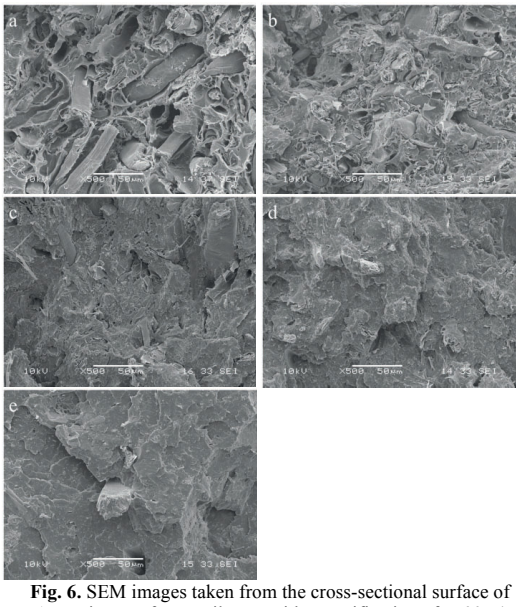
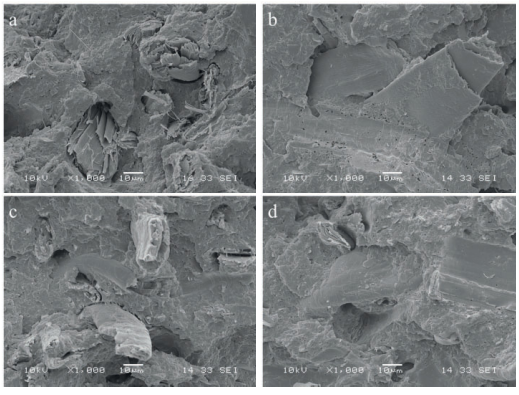


Fig. 6. SEM images taken from the cross-sectional surface of PLA specimens after tensile test with magnification of x500: a) PLA-BSKP; b) PLA-LPB; c) PLA-ONP; d) PLA-ONP/Fibrous sludge; e) PLA-Fibrous sludge

Compatibility of all tested fibres with the PP matrix seemed to be quite good, and large holes between fibres and matrix are not visible (Figure 7). Probably the use of a coupling agent improved the fibre-matrix adhesion to such an extent that the hydrophilic/hydrophobic natures of different fibres did not affect the adhesion. Uniform fibre dispersion and good fibre adhesion might explain the minor differences in the mechanical properties of PP-fibre composites between different fibres.



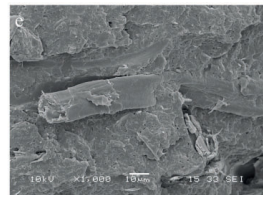


Fig. 7. SEM images taken from the cross-sectional surface of PP specimens after impact test with magnification x1000: a) PP-BSKP; b) PP-LPB; c) PP-ONP; d) PP-ONP/Fibrous sludge; e) PP-Fibrous sludge

4. CONCLUSIONS

In PLA composites, recycled fibres provided higher mechanical properties for PLA composites than native softwood kraft pulp fibres, even though recycled fibres consisted of about 20% less long reinforcing fibres. The highest mechanical properties were achieved with LPB fibres, which were more hydrophobic than kraft pulp fibres. The used ONP fibres were non-deinked, leading to dark color of the composite. Use of deinked fibres would allow the composites to be colored more easily. In a PP-matrix the differences in mechanical properties between different fibre types were relatively small. Uniform fibre dispersion and good fibre adhesion of all fibre types might be the explanation for this. The fibres from LPB, being more hydrophobic, seemed to improve the composite properties clearly. Fibrous sludge decreased the mechanical properties of composites but could be considered as cheap filler in cases where mechanical properties are not crucial.

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PUBLICATION V

Foamability and viscosity behaviour of extrusion foamed PLA - pulp fiber composites

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Journal of Applied Polymer Science 136 (41) (2019) 48202
https://doi.org/10.1002/app.48202

Journal of Applied Polymer Science

Foamability and viscosity behavior of extrusion foamed PLA-pulp fiber biocomposites

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ABSTRACT: This study addresses the effect of fiber reinforcement, chain extension, and physical foaming agent type on foam morphology and viscosity behavior of pulp fiber reinforced poly(lactic acid) (PLA) biocomposites. PLA reinforced with 0, 10, and 20 wt % of bleached kraft pulp fibers with and without chain extender were foamed using two different physical foaming agents (carbon dioxide and isobutane) by extrusion foaming. Densities, foam morphologies, and viscosities were systematically analyzed and compared from the produced foams. As a conclusion, low-density foams are produced with both foaming agents and fiber levels, fiber addition limiting cell growth. Isobutane provides better dimensional stability with narrower cell size distribution, whereas carbon dioxide enables lower foaming temperature. Chain extension is essential to achieve foam with low density and good cell structure. Contrary to nonchain extended PLA, addition of fibers reduced the viscosity of chain extended PLA. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 48202.

KEYWORDS: biocomposite; foaming; foam morphology; poly(lactic acid); pulp fibers; wood-based fibers

Received 12 April 2019; accepted 11 June 2019

DOI: 10.1002/app.48202

INTRODUCTION

Recently, sustainable and biobased material solutions have gained significant interest due to their reduced environmental impact. New legislative initiatives such as the EU plastic strategy, waste directives, and circular economy package are pushing the adoption of renewable, reusable, and recyclable materials. In addition, compostable solutions support the transition to circular economy, providing alternative end-of-life possibilities for applications such as biocomposites or lightweight solutions that are challenging to recycle due to multimaterial compositions or nonprofitable logistics. Currently, various biobased and biodegradable thermoplastic materials are commercially available: the major players in the markets are starch-based blends, poly(lactic acid) (PLA), and polyhydroxyalkanoates.[1] Increasingly, biodegradable or compostable solutions are used in applications such as biodegradable biowaste bags, multilayer packaging, mulch films, and single-use plastic cutlery.

By decreasing the weight of a material, it is possible to reduce its ecological footprint while at the same time optimizing material, energy, and cost performance. Plastic foams (also known as polymer foam, expanded plastics, or cellular plastics) are polymeric materials with cellular structure. Cellular structure is formed from gaseous phase and solid phase. This kind of structure reduces the apparent density of a material.[2] With foams, much lower densities and wider density ranges can be archived than with traditional solid materials. Therefore, they are useful for light structures such as flotation, automotive parts, and packaging. Foams typically have low thermal conductivity, which makes them ideal for insulation purposes. Foam can also have varying ranges of stiffness and therefore they can be used in comfortable cushioning or in stiff structures. Generally, foams have low strength but high toughness, which makes them useful in energy absorbing application.

Foaming of biopolymers has been addressed in several studies.[3–6] Especially, PLA has gained a lot of interest for foam applications due to its biobased and compostable nature, decent mechanical properties, and variation possibilities.[7–9] However, some challenges in the production of highly expanded PLA foams include its narrow processing temperature window and low melt strength causing insufficient cell growth due to cell wall ruptures and cell coalescence.[10] Melt strength of PLA can be improved by branching of the polymer, enabling generation of highly expanded foams.[11] Due to improved melt strength, molecular branching is shown to influence the cellular structure of PLA promoting generation of a large number of small cells.[12]

Typically, biocomposites refer to plastic materials which have been reinforced with natural fillers or fibers. A typical product of the first

generation of biocomposites is wood plastic composite (WPC) decking, in which wood flour has been used as filler. Wood flour reduced price and provides stiffness but does not improve other physical properties.[13] However, in recent years, the use of wood-based fibers from papermaking industry as composite reinforcement has gained significant interest. Contrary to wood flour, wood fibers can provide other material improvements such as improved tensile and impact strength[14,15] together with high availability and low cost. Consequently, biocomposite materials based on wood pulp fibers have already entered the markets.[16–18] Wood fiber based biocomposites are typically used in injection-molded products, but to accelerate the market uptake, new production technologies, and applications are needed.

Solid biocomposites, such as WPCs, have found applications areas in many industries, and while they represent significant business opportunities in material and energy efficiency, some material shortcoming needs to be considered, such as high density and poor mechanical workability. Many of these shortcomings of solid biocomposites can be addressed by changing the architecture through foaming, if provided by suitable foaming technique and proper cellular structure.[19,20] This opens application areas such as packaging, construction, and automotive for this new class of materials.

However, wood fiber composites have certain challenges in foaming process. Especially, the moisture in the wood requires attention in extrusion foaming. Water has poor solubility in polymers and it will remain as a separate phase during processing and evaporate immediately after the pressure is released without the need for nucleation. High amounts of moisture can cause high cell size distribution or exacerbate bubble rupture, which can lead to severe gas loss; therefore, minimal moisture content is required for optimal cell structures.[21–23] Simplified, wood fibers can contain water in three forms: free, bound, and through chemical decomposition. While free water is liquid and relatively easily removed, bound water is more difficult as it is held in the structure by intermolecular forces. Prolonged heating of wood fibers can additionally generate water (and volatile organic compounds, (VOCs)) through chemical decomposition.[23,24] It has been shown by Rizvi *et al.*[23] that while free water can be removed by oven drying, the more tightly bonded moisture can be released at elevated processing temperatures, and that this moisture content alone can be enough to cause foaming of wood fiber composites. In addition to moisture, wood also contains other extractives that can be volatilized at high temperatures, possibly disturbing the foaming phenomena. Compared to wood fibers, bleached kraft pulp fibers contain less extractives,[25] which should lead to lower emission of volatiles during processing and therefore less deteriorated cell morphologies.

Extrusion foaming of wood-based biocomposites has received some attention in the literature so far. Studies have mainly been targeted toward fossil-derived matrix polymers such as polypropylene,[26] high-density polyethylene,[27] polystyrene,[23] and poly(vinyl chloride),[19] mostly using wood flour or wood fibers as reinforcement. Some studies have also been performed with wood flour–PLA foam combinations.[28–30] A limited number of published studies have focused on foaming of cellulose or pulp fiber reinforced PLA.[31–36]

Physical foaming of fiber reinforced PLA in a batch process has been described by Neagu *et al.*[33] where they achieved wood fiber-reinforced PLA composites foams using CO_2, but the foams were formed using PLA fiber and wood fiber preforms resembling the slurry processing used in paper production. Similarly, Bergeret and Benezet[34] introduced PLA foams reinforced with 25 wt % of cellulose fibers, but the foaming was performed with chemical foaming agents, thus the foaming method differ from physical foaming.

An example of physical foaming of PLA cellulose composite was described by Geissler *et al.*[35] where they investigated the influence of the addition of 2–6 wt % of cellulosic TENCEL fibers on mechanical and foam properties of PLA foams. The study concluded that cellulose fibers acted as nucleating agent for PLA in foaming, improving the cell morphology. In addition, Bocz *et al.*[36] showed that addition of 5 wt % of cellulose fibers promoted cell nucleation, but also led to less uniform cell structure and increased open cell ratio due to weak fiber matrix adhesion and fiber dispersion. On the other hand, Bocz *et al.* concluded that cellulose fibers provided a wider processing window for PLA foam production with lower applicable processing temperature.

Koyama *et al.*[31] studied extrusion foaming of cellulose fiber reinforced PLA using CO_2 as physical foaming agent. The addition of 20 wt % of cellulose fibers suppressed expandability and increased cell density of PLA. By decreasing die temperature, both cell density and foam density of PLA decreased. According to the authors, this was a result of the viscosity decrease during extrusion foaming, which was explained by polymer degradation. The viscosity decrease was higher when wood fibers where present, which was speculated to be due to increased degradation of the PLA matrix during processing.

Ding *et al.*[32] concentrated on the development of cellulose fiber reinforced PLA foams using injection molding process. They discovered that cellulosic fibers, acting as nucleating agent, increased crystallization temperature, and crystallinity of the matrix resulting in a more uniform cell structure.

The aim of this study was to investigate the effect of pulp fibers, chain extension, and physical foaming agent type on foam morphology and viscosity behavior of extrusion foamed PLA biocomposite foams. Generally, chain extension was found to be essential, even though with carbon dioxide, it is possible to produce low-density foams also without chain extension utilizing foaming temperatures near the crystallization temperatures. For the first time, pulp fiber reinforced PLA foams are compared using carbon dioxide and isobutane as physical foaming agents. With both foaming agents, it was possible to produce low density biocomposite foams even with 20 wt % fiber content, although isobutane provided smoother surface and better dimensional stability with narrower cell size distribution. Without chain extension, pulp fibers increased the viscosity of PLA, but in the case of chain-extended PLA, the addition of fibers was observed to reduce the viscosity of the chain-extended materials. The use of carbon dioxide as foaming agent resulted in the lowest foaming temperatures, indicating higher viscosity reduction effect than with isobutane.

Overall, the research provides valuable information of the foaming behavior of pulp fiber reinforced PLA, including the use of isobutane as foaming agent. In wider aspect, the study establishes new opportunities for lightweight applications of pulp fiber

composites, currently focused almost exclusively on solid injection molded applications.

EXPERIMENTAL

Materials and Preparation

Materials. Foaming grade PLA 8052D purchased from NatureWorks LLC was used as the matrix polymer. Bleached hardwood (birch) kraft pulp fibers (average fiber length 0.9 mm and aspect ratio 40)[37] were used as the reinforcing material and were provided by a Finnish pulp manufacturer. Multifunctional epoxide chain extender (CE) JONCRYL 4368-CS from BASF was used to increase melt strength of PLA. In the foaming process, isobutane (IB) and carbon dioxide were used as foaming agents. They were purchased from the Linde Group and AGA Oy Ab, respectively. As a nucleating agent, Finntalc M05SL with a median particle size of 2.2 μm was used.

Material Preparation, Twin-Screw Extrusion. PLA granulates were compounded with pulp fibers and CE according to Table I by using Berstorff ZE25x48D corotating twin-screw extruder. The processing setup and temperature profile is presented in Figure 1. The pure PLA reference material was also processed with the twin-screw extruder to give it the same thermal history as for the other materials. The CE was fed in as a 30% PLA masterbatch. The masterbatch material was produced with similar setup as shown in Figure 1, difference being that only PLA 8052D was fed at the start of the extruder and 30 wt % pure CE power was fed at the end of the extruder. Additionally, the temperature at the last two zones was 170 °C and the die temperature was 180 °C. To minimize side reactions, CE was introduced at the end of the extruder in both cases. Final dosage of the CE in the compounds (0.7%) was based on NatureWorks LLC's suggestion for PLA 8052D. The extruded material was cooled using a water bath and then granulated. Prior to compounding, the pulp fibers (F) sheets were shredded to ease feeding into the twin-screw extruder. PLA and the masterbatch were dried at 75 °C in vacuum overnight and the fibers were dried at 50 °C overnight. In Figure 2, the effect on fibers on the color of the material is presented. The increasing fiber content changed the transparent/white color of the PLA to light beige color. The color increased in saturation with higher fiber content. To minimize fiber burning/oxidation, melt temperatures were kept well below 200 °C.

Extrusion Foaming. Foam samples were prepared with a Brabender Plastograph EC Plus, equipped with 19 mm single-screw extruder, melt pump, and melt cooler. The melt cooler was a static mixer type with oil tempering. Foaming agent was pressurized and injected with a Teledyne ISCO Dual pump continuous flow system. The foaming agent amount was maintained at 5 wt %, based on the polymer content of a material. Two different physical foaming agents were utilized: isobutane and carbon dioxide.

Table I. Produced Material Compositions

Abbreviation	Pulp fiber amount (wt %)	CE amount (wt %)
PLA	0	0
PLA-10F	10	0
PLA-20F	20	0
PLA-CE	0	0.7
PLA-CE-10F	10	0.7
PLA-CE-20F	20	0.7

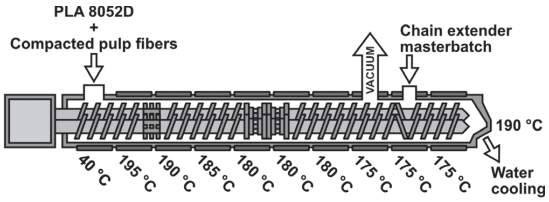

Figure 1. Twin-screw extruder setup.

In the extruder, a foaming screw configuration was used with low inner diameter at the foaming agent injection point to prevent back flow of the foaming agent. As a nucleating agent, 0.1 wt % of talc was used, dusted on to the material via bag mixing. The polymer material feed rate was kept constant at 6.6 cm^3 min^{-1}, which equals approximately 6.5–7 g min^{-1} depending on material composition. The complete foam processing setup is presented in Figure 3.

To activate the CE, temperatures where maintained above 200 °C at the end of the extruder barrel. The extruder and melt pump temperatures were kept constant and melt cooler and die temperatures were changed. The melt cooler temperature was kept approximately 10 °C higher than the die temperature. The target for the foaming temperature was to find the lowest possible die temperature, based on ocular estimation that produced low-density foam with a good cell structure. The final foaming temperature was typically just above the temperature where the die would clog up due to material crystallization. Materials were dried at 60 °C under vacuum overnight prior to foaming.

Characterization

Density Measurement. Densities of the foamed samples were determined with liquid submersion technique using reverse osmosis purified water as the liquid media. Surfactant was used to reduce the surface tensions of the water. At least three parallel density measurements were made from each foam sample. Weighing was performed with Mettler AT261 Delta Range scale.

Scanning Electron Microscopy. Microscopic imaging of the foamed samples was performed with a JEOL JSM-6360LV scanning electron microscope (SEM). A small section of the foam extrudate was frozen in liquid nitrogen and fractured. The fracture surfaces were then gold coated with Bal-Tec Balzers SCD 050 sputter coater. Acceleration voltage of 10 kV was used and the images were constructed from secondary electrons.

Tomography. The three-dimensional (3D) foam structure, void fraction, and bubble size distribution of the foamed samples were studied using micro-computed tomography (μ-CT). Tomographic analyses were performed on 10 wt % filled materials. The sample length was approximately 10 mm and was cut from the collected extrudates. The tomographic images were acquired with an

Figure 2. Effect of fibers on the material color. [Color figure can be viewed at wileyonlinelibrary.com]

Xradia μ-CT-400 tomograph, which is a standard cone-beam tomography with additional optical magnification of the projection images. The scans were performed with 40 kV acceleration voltage and 4 W electron beam power. Total of 1585 projection images were acquired with 3 s exposure time. 3D tomographic volume images were reconstructed from the projection images via the device manufacturer's proprietary programs. Image visualizations were made with Avizo Fire 8.1 software (FEI Technologies Inc., Hillsboro, OR, USA).

The tomography stacks where analyzed with ImageJ (version 1.51k) and thresholded using Otsu's method.[38] A subsample of 210 × 210 × 1978 pixels completely enclosed within the volume of the sample was cropped from the thresholded stacks. From the subsample, the void fraction (total volume of voids to solid material) was estimated. Bubble size distribution was estimated from the subsample with the local thickness calculation.[39]

Capillary Rheometry. GÖTTFERT Rheograph 6000 capillary rheometer was used to determine the rheological behavior of the six prepared materials. Before the rheological evaluation, the materials were processed with the foaming extruder (similar to the setup in Figure 3 but without foaming agent) in order to activate the CE in the PLA matrix. The materials without CE where also processed with the same foam extruder setup in order to give them same the thermal history as the samples with CE. The capillary rheometry was carried out at 190 °C with 6 min preheating time and by using a 1/30 mm die. Shear rate range was from 30 to 1000 s^{-1}. Only apparent values were recorded. The data were subsequently fitted using the Carreau–Yasuda equation[40] for evaluating purposes.

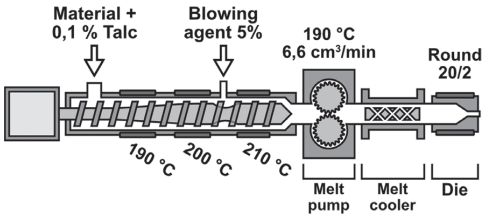

Figure 3. Foam extrusion setup.

RESULTS AND DISCUSSION

In the study, the effect of fibers, chain extension, and physical foaming agent type (CO_2 or isobutane) on foamability of PLA has been considered in two respects: (1) foam morphology and (2) viscosity behavior.

Foam Morphology

Effect of Fibers. When fibers are added to the PLA matrix, the relative amount of PLA is reduced as it has been partially replaced by a non-foaming material. Additionally, since the foaming agent was dosed according to the PLA content during the foaming process, it is to be expected that the materials containing fibers do not achieve as low densities or high expansions as material without fibers. Moreover, the cellulose fibers are expected to mechanically restrict the foamability of PLA in some extent, by long-range anchoring of the polymer matrix, and in addition contribute a small increase in the density on their own, due to possessing an inherent higher density than PLA (1.4 vs. 1.24). This is reflected in Figures 4 and 5, where samples with higher amounts of fibers have produced narrower strands and with higher density (Table II). This behavior is independent of addition of CE or foaming agent type. However, it was found that this effect was relatively minor up to a 10 wt % fiber content. The density was increased from 0.055 g cm^{-3} (PLA-CE) to only 0.07 g cm^{-3} (PLA-CE-10F). When fiber content was increased to 20 wt % (PLA-CE-20F), the density was increased above 0.1 g cm^{-3} which can still be considered as a low-density foam.

SEM imaging of foamed samples, illustrated in Figures 6 and 7, show that the presence of fibers reduces the average cell size and increase the cell density, as was also observed by previous studies.[31,32,36] In addition, the presence of fibers seems to hinder cell growth, which was also noted by Koyama *et al.*[31] Since the cells stay small, they also are less prone to rupturing and coalescing, which would increase average cell size and cell size distribution. In addition, the fibers introduce more heterogeneous nucleation sites which promote cell nucleation and cause smaller average cell size to form. With 20 wt % of fiber content, the average cell structure is more deteriorated than with 10 wt % of fibers, but still, a well expanded foam structure is achieved.

Effect of CE. Chain extension of PLA causes branching and increases molecular weight both of which increase the melt strength of PLA. When material has high melt strength, the

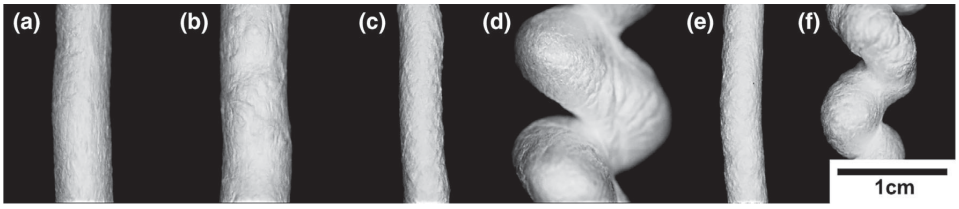

Figure 4. Side profiles from the produced foams without CE. (a) PLA-IB, (b) PLA-CO_2, (c) PLA-10F-IB, (d) PLA-10F-CO_2, (e) PLA-20F-IB, and (f) PLA-20F-CO_2.

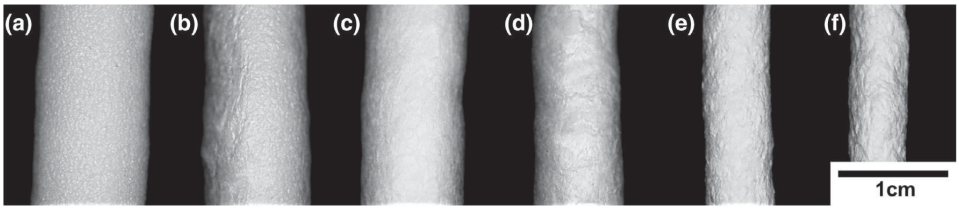

Figure 5. Side profiles from the produced foams with CE. (a) PLA-CE-IB, (b) PLA-CE-CO_2, (c) PLA-CE-10F-IB, (d) PLA-CE-10F-CO_2, (e) PLA-CE-20F-IB, and (f) PLA-CE-20F-CO_2.

forming cells can hold their shape and resist rupture better before the cell structure has time to stabilize.[41] It is quite apparent based on density measurements (Table II), foam strand profiles (Figures 4 and 5), and SEM images (Figures 6 and 7) that in order to achieve foam with a low density and good cell structure, chain extension of PLA is essential. In some of the produced foam samples, lack of CE (i.e., PLA and PLA-20F) leads to cell structures that have either collapsed or the cells have ruptures so severely that individual cells are hard to distinguish.

However, with carbon dioxide, it is possible to produce low-density foams from the studied biocomposites even without chain extension utilizing foaming temperatures near the crystallization temperature. This technique was also used by Li *et al.* on a batch foaming process.[42] Carbon dioxide is known to induce crystallization in PLA.[43] In a way, the crystals can act as melt strength increasing domains by locking the structure, and act as cell nucleation sites. At these low temperatures, very low-density foams (Table II) can be achieved but the foam strand is curled due to nonstable process conditions [Figure 4(d,f)]. With higher foaming temperature (Table III), stable foam strand can be produced more easily [Figure 4(b)] but without achieving as low densities. The cell structure is also much more prone to rupturing and coalescing producing very nonuninform foam due to the inherent low melt strength. It is clear that the absence of CE complicates the foaming process immensely and the process in these conditions is highly unoptimized and can give inconsistent results. These observations are therefore more related to the foaming process than material performance.

Table II. Density of the Prepared Foam Samples

Material	Isobutane (g cm^{-3})	Carbon dioxide (g cm^{-3})
PLA	0.41	0.38
PLA-10F	0.61	0.10
PLA-20F	0.62	0.40
PLA-CE	0.06	0.05
PLA-CE-10F	0.07	0.07
PLA-CE-20F	0.13	0.14

Effect of Foaming Agent. Both isobutane and carbon dioxide can be used to produce low-density foams but some differences in the developed cell structures can be noticed. Illustrated in Figure 5, there is an indication that isobutane produces foam strands with a smoother surface and better dimensional stability than carbon dioxide. Similar behavior with PLA and carbon dioxide was already observed by Reignier *et al.*[7] The shrinkage of the foams produced with carbon dioxide is caused by negative pressure inside the foam cells since carbon dioxide has higher permeation through PLA than nitrogen and oxygen.[44] In other words, carbon dioxide permeates out of the foam cells faster than air can replace it. Isobutane, however, with its larger molecular weight, permeates more slowly through the cell walls. Consequently, the pressure inside the cells is either positive or at equilibrium with the surrounding air pressure.

The shrinkage effect is also partially related to the cell structure. The cell structure in the prepared foam is mainly closed cell. Therefore, the gasses need to migrate through the cell walls. If the structure was open celled, the gasses could transfer more easily.

The tomographic imaging performed on PLA-CE-10F foams reveals that with isobutane narrower cell size distribution was achieved than with carbon dioxide (Figure 8). The void size peak in the normalized tomography data was at 25 for both foaming agents but the amount of large cells was much greater on the sample prepared with carbon dioxide which increased the average number. This is also visible from the tomography slice images

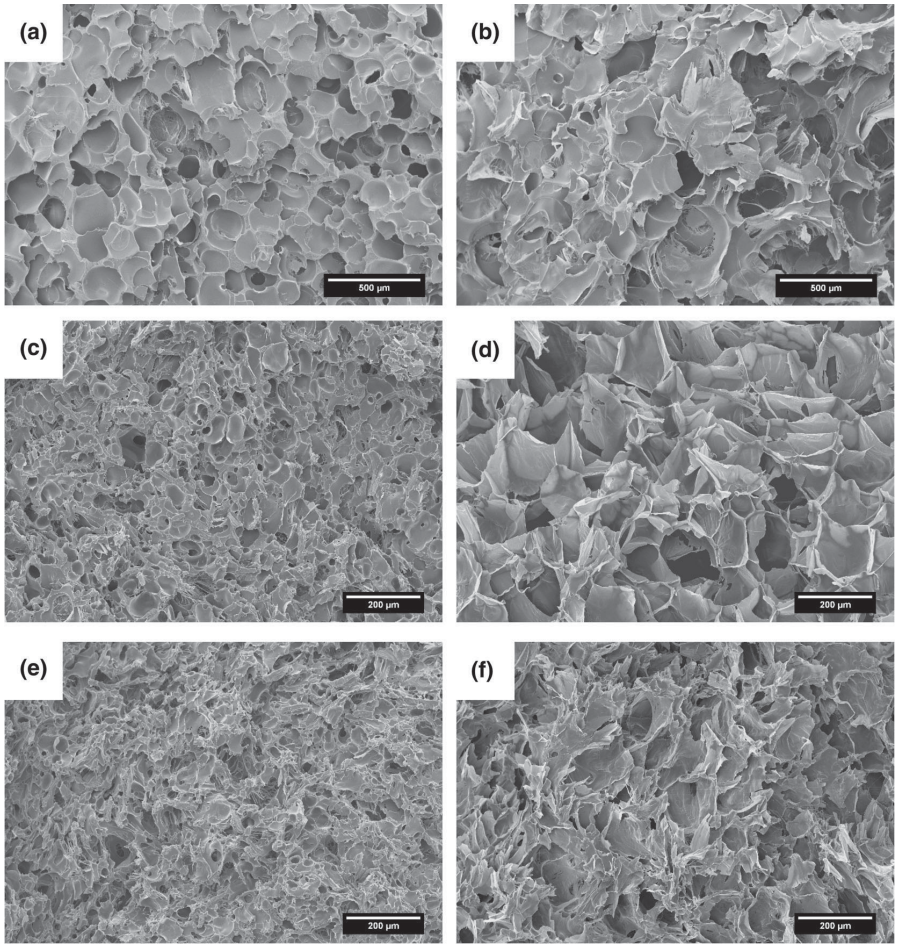

Figure 6. SEM pictures of prepared foams without CE. (a) PLA-IB (50×), (b) PLA-CO_2 (50×), (c) PLA-10F-IB (100×), (d) PLA-10F-CO_2 (100×), (e) PLA-20F-IB (100×), and (f) PLA-20F-CO_2 (100×).

shown in Figure 9. Due to the high diffusion rate of CO_2, it is likely that cell coarsening has occurred. In cell coarsening, gas from small cell diffuses into large cell generating even larger cell while the small cell collapses. Once large cell has formed, it is possible that they can then rupture and coalesce, forming even larger cells. It can be seen from Figure 7(c,d) that the foam made with carbon dioxide gives an indication of containing more ruptured cells.

Viscosity

Effect of Fibers. The capillary rheology results (Figure 10) show that the addition of pulp fibers to nonchain extended PLA increases the viscosity of the material. The viscosity increase is most noticeable in the low shear rate region (<200 1/s) where the pulp fibers present a greater resistance to the flow since they are not totally aligned with the direction of the flow. The high shear rates (>500 1/s) induce increased fiber alignment, which lessens the effect of fibers on the viscosity.

Effect of CE. It is well established that usage of multifunctional epoxide-based CE increases the viscosity of PLA, by increasing the average molecular weight.[45] This effect can be seen in Figure 10 where the chain extended PLA samples have significantly higher viscosities than their nonchain extended counterparts.

However, contrary to the observation with nonchain extended PLA, the addition of fibers reduced the viscosity of the chain extended PLA. In fact, the material with the highest fiber content had the lowest overall viscosity from the chain extended materials. The reduced viscosity must be an effect in the matrix, and while not fully understood, can be interpreted in a few different ways. A first possibility could be that the combination of CE and pulp fiber causes a degradation on the PLA, as this was not seen in the nonchain extended samples. Potentially, involving residual moisture in the fibers, despite the drying regime. Another possibility could be the CE reacts with the pulp fibers instead of the PLA molecules, limiting the potential molecular weight recovery of the PLA. In other words, the PLA and

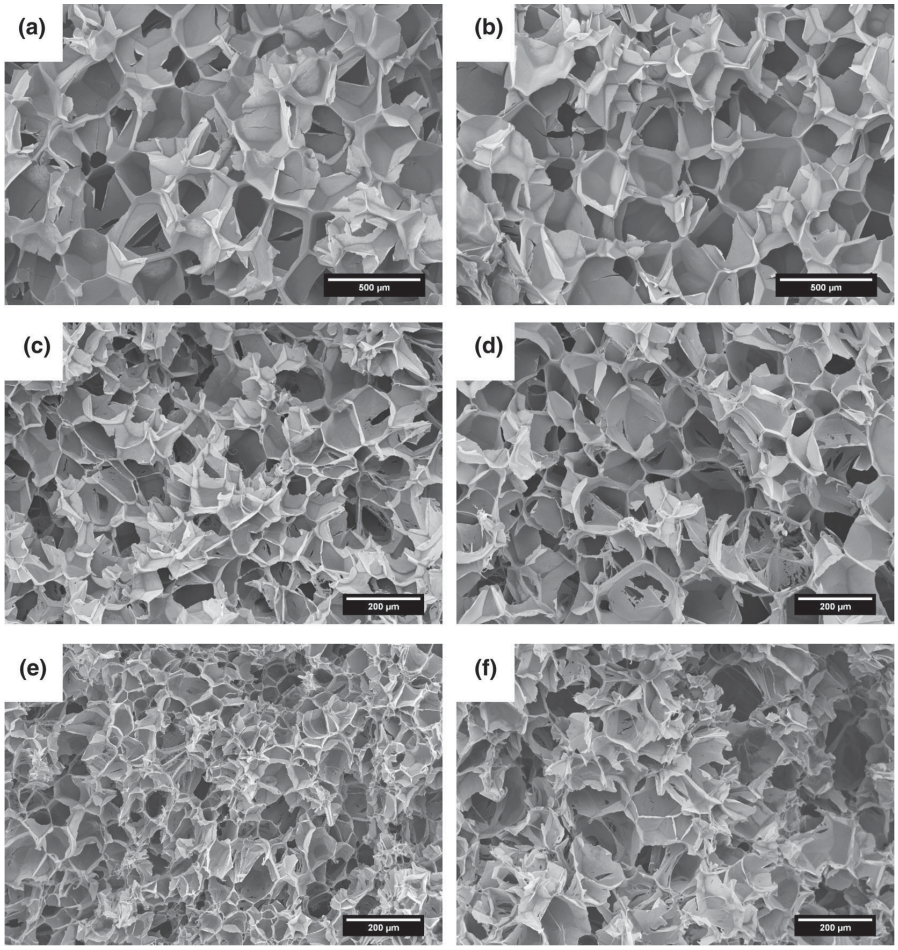

Figure 7. SEM pictures of prepared foams with CE. (a) PLA-CE-IB (50×), (b) PLA-CE-CO_2 (50×), (c) PLA-CE-10F-IB (100×), (d) PLA-CE-10F-CO_2 (100×), (e) PLA-CE-20F-IB (100×), and (f) PLA-CE-20F-CO_2 (100×).

fibers are competing against each other to react with the CE. It is also possible that the observed effect is a combination of both mechanisms.

Table III. Effect of Foaming Agent on the Foaming Temperature

Material	Isobutane (°C)	Carbon dioxide (°C)
PLA	125	123
PLA-10F	127	115
PLA-20F	127	120
PLA-CE	135	133
PLA-CE-10F	138	135
PLA-CE-20F	130	130

Effect of Foaming Agent. Foaming agent is known to reduce the viscosity of a polymeric material since they essentially work as plasticizer during the foaming process increasing the free volume.[46,47] To achieve low-density foams, the viscosity reduction effect of foaming agent is countered by lowering the temperature of the melt. Foaming temperature is therefore affected by the foaming agent and thus the foaming temperature is an indicator about the behavior of the polymer-foaming agent system.

Since lower foaming temperatures were systematically reached with carbon dioxide (see Table III), it can be estimated that the viscosity reduction effect of carbon dioxide was greater than that of isobutane. If no chain extension was used, it was able to reach significantly lower temperatures than with carbon dioxide but with the expense of stable foam formation [see Figure 4(d,f)]. With higher temperature foaming stability similar to isobutane was achieved with carbon dioxide [see Figure 4(a,b)]. Carbon dioxide lowers the crystallization temperature of PLA significantly[48] and the sample foams were produced

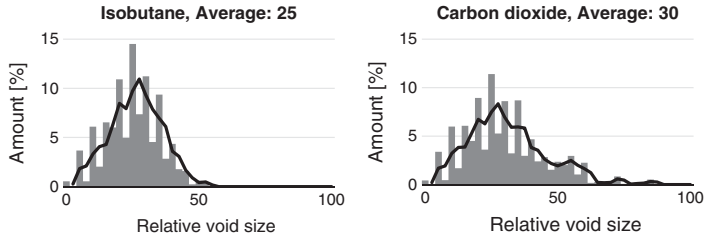

Figure 8. Normalized void size distribution determined via μ-CT for PLA-CE-10F foamed with isobutane and carbon dioxide.

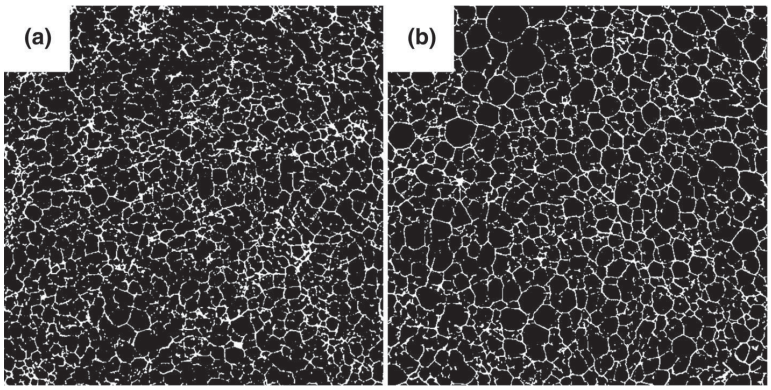

Figure 9. Tomography slice image. (a) PLA-CE-10F-IB and (b) PLA-CE-10F-CO_2.

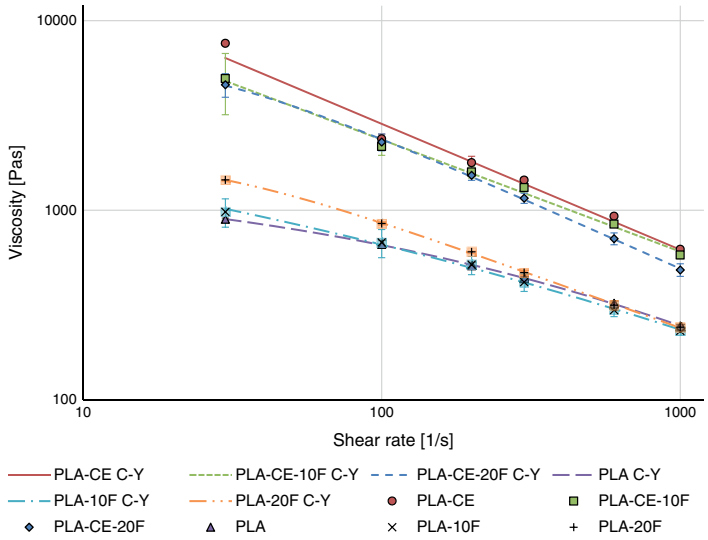

Figure 10. Rheological behavior determined with capillary rheometer at 190 °C. Error bar is a standard deviation from three parallel measurements. Data fitted with Carreau–Yasuda equation (C–Y). [Color figure can be viewed at wileyonlinelibrary.com]

very near to the crystallization temperature. The unstable nature of the foaming is related to some parts of the PLA extrudate crystallizing on the die walls (i.e., stick–slip).

CONCLUSIONS

In the study, it was concluded that it is possible to produce low-density foams with 10 and 20 wt % pulp fiber reinforced PLA biocomposites both with CO_2 and isobutane as physical foaming agents. Addition of fibers, however, reduced foam expansion and average cell size. Generally, of the studied compositions, in order to achieve low-density foams with good cell structure, chain extension of PLA was essential. Nevertheless, utilizing carbon dioxide, it was also possible to produce low-density foams even without chain extension, utilizing foaming temperatures near the crystallization temperature. However, with this method the foam cell structure was poor.

There is an indication that isobutane produces foam strands with a smoother surface and better dimensional stability than carbon dioxide. The shrinkage of the foams produced with carbon dioxide is caused by negative pressure inside the foam cells, due to carbon dioxide possessing a higher permeation through PLA than nitrogen and oxygen. Isobutane achieved a narrower cell size distribution than carbon dioxide, which is probably due to high diffusion rate of CO_2, resulting in cell coarsening. Despite the differences in the dimensional stability and cell size distribution, both isobutane and carbon dioxide managed to produce low-density foams with the chain extended material.

Confirming earlier observations, the addition of pulp fibers to nonchain extended PLA increases the viscosity of the PLA, as also observed by the addition of a multifunctional epoxide-based CE. However, contrary to the observation with nonchain extended PLA, the addition of fibers was observed to reduce the viscosity of the chain extended PLA. We postulate that this may be caused by two potential mechanisms. Either that the combination of the CE and pulp fiber causes a degradation on the PLA molecular weight, or alternatively, that the CE has a competing reaction with the fibers, reducing the potential molecular weight recovery of the PLA.

The lowest foaming temperatures were systematically reached with carbon dioxide, indicating that the viscosity reduction effect of carbon dioxide was much greater than that of isobutane.

ACKNOWLEDGMENTS

The authors would like to thank the CLIC Innovation Ltd., Finland, project New Fiber Products (NewFP) for partial funding to carry out this research. In addition, the authors would like to thank colleagues Hannu Minkkinen and Mirja Nygård from VTT, as well as Arttu Miettinen from University of Jyväskylä for helping with practical work and analyses.

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